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molten potassium hydroxide in its action on organic substances, the result of which can be accepted only as corroborative evidence in questions of constitution when harmonising with those from sources less under suspicion.

EXPERIMENTAL.

A preliminary experiment showed that the action of fused potassium hydroxide on phenylglyceric acid does not give rise to effervescence until a temperature approaching 150° is reached, when the odour of toluene is noticeable; thereafter, at about 180°, the action becomes difficult to control, and the pasty mass remaining after nine minutes have elapsed in reaching 200° contains potassium benzoate and oxalate. More precise conditions were therefore defined.

At a Temperature of 160—170°.—Ten grams of phenylglyceric acid with 50 grams of potassium hydroxide and 20 c.c. of water in a retort connected with a condenser were heated during fifty-four minutes by a bath of fusible metal at 160—170°, action at first being very vigorous. Toluene (3·3 grams) passed over in the steam and, when isolated, distilled completely at 110—111° (Found : C = 91·3; H = 8·8. C_7H_8 requires C = 91·3; H = 8·7 per cent.). The residue in the retort having been dissolved in water, aliquot parts of the solution were examined separately and quantitatively for benzoic, and for oxalic and formic acids, the amounts estimated being 0·68, 3·4, and 0·11 gram respectively; the presence of acetic acid was demonstrated qualitatively. Hence the toluene and oxalic acid were produced in equivalent amounts, and the extent of conversion was about 68 per cent.

At a Temperature of 240—250°.—Potassium hydroxide (50 grams) and water (20 c.c.) in a nickel crucible were heated by fusible metal, and when the temperature had reached 240—250° phenylglyceric acid (10 grams) was added in small quantities with continued stirring during twenty minutes, liberation of benzoic acid vapour being recognisable. The cold, faintly green product was dissolved in 150 c.c. of water and acidified with 68 c.c. of hydrochloric acid, when benzoic acid was precipitated; the quantity, making allowance for solubility in water, amounted to 4 grams, and the filtrate contained 3·1 grams of oxalic acid. Thus the acids were produced in approximately equivalent amounts, the deficit of benzoic acid being doubtless due to volatilisation during fusion; the extent of conversion was about 60 per cent.

At 170—180°, *under Reduced Pressure.*—Phenylglyceric acid (5 grams), potassium hydroxide (?5 grams), and water (10 c.c.) were

heated in a distilling flask which was evacuated through a condenser. By controlling the temperature of the castor-oil bath at 170—180°, the pressure was maintained during ten minutes at 25 mm., but this reduction was not reached until almost all the water had been removed. The oil which distilled was negligible, and the colourless residue in the flask having been extracted with water and acidified, *iso*hydrobenzoin (1·9 grams), benzoic acid (0·2 gram), and oxalic acid (1·2 grams) were recognised. Thus the quantity of *iso*hydrobenzoin indicated a conversion of 65 per cent., but the amount of oxalic acid, whilst exceeding one equivalent, fell somewhat short of that corresponding with two molecular proportions.

Since benzoic acid and *iso*hydrobenzoin melt at the same temperature (121°), identity of the latter substance was established by analysis and by determination of molecular weight in boiling acetone (Found: C = 78·60; H = 6·59. M = 213. $C_{14}H_{14}O_2$ requires C = 78·50; H = 6·54 per cent. M = 214). The diacetyl derivative melted at 117—118° (Found: C = 72·29; H = 6·07. $C_{18}H_{18}O_2$ requires C = 72·48; H = 6·04 per cent.).

CHEMICAL LABORATORY,
   ST. THOMAS'S HOSPITAL, S.E.1.   [*Received, September 24th,* 1921.]

CXCIV.—ortho-*Chlorodinitrotoluenes. Part IV.*
2-*Chloro*-3 : 4-*dinitrotoluene.*

By GILBERT T. MORGAN and THOMAS GLOVER.

IN an earlier communication (T., 1920, **117**, 784) the number of known *o*-chlorodinitrotoluenes was increased from two to four, these isomerides being obtained by nitrating *o*-chlorotoluene or its mononitro-derivatives. The remaining two isomerides may also occur to a small extent among the crude nitration products, but hitherto these compounds have escaped detection.

2-Chloro-3 : 4-dinitrotoluene (III), melting at 89°, has now been prepared indirectly by the Sandmeyer reaction from 3 : 4-dinitro-*o*-toluidine (II), a base recently described by Brady and Williams (T., 1920, **117**, 1137), and with the isolation of this new isomeride the three theoretically possible *o*-dinitro-derivatives of *o*-chlorotoluene have been obtained, so that the reactions of this set of closely related isomerides may be compared.

· When treated with ammonia or aniline, 2-chloro-3 : 4-dinitrotoluene readily furnishes an amine in which the 3-nitro-group is

replaced quantitatively by the basic radicle. *2-Chloro-4-nitro-m-toluidine* (VI) and *2-chloro-4-nitro-N-phenyl-m-toluidine* (IV) are obtained respectively, and the orientation of the amino- and phenylamino-groups has been demonstrated by the methods summarised in the following diagram :
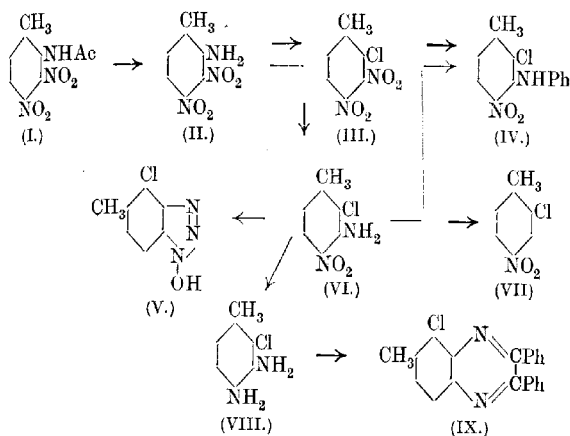
It is noteworthy that the two consecutively substituted isomerides, 2-chloro-3 : 4-dinitrotoluene and 2-chloro-5 : 6-dinitrotoluene, having the two contiguous nitro-groups at one end or the other of the consecutive series of substituents each lose the interior (3- or 6-) nitro-group only and give rise to one amine (IV and VI) when treated with ammonia or aniline. On the contrary, 2-chloro-4 : 5-dinitrotoluene, which has its contiguous nitro-groups separated from the other substituents, furnishes on treatment with ammonia a mixture of amines, as recently demonstrated (this vol., p. 1537), showing that each nitro-group in this isomeride is possessed of a certain degree of lability.

Hydrazine hydrate reacts with 2-chloro-3 : 4-dinitrotoluene giving *4-chloro-1-hydroxy-5-methyl-1 : 2 : 3-benzotriazole* (V), in which it is assumed, from analogy with the condensation with ammonia, that this diamine replaces the 3-nitro-group and condenses with the 4-nitro-group to complete the triazole ring. *2-Chloro-3 : 4-tolylenediamine* (VIII), obtained by the reduction of 2-chloro-4-nitro-*m*-toluidine, gives the typical reactions of an ortho-diamine, condensing with benzil to yield 5-chloro-2 : 3-diphenyl-6-methylquinoxaline (IX).

These condensations show that the two nitro-groups in 3 : 4-

3 N 2

dinitro-*o*-toluidine are actually in *ortho*-positions to one another, and since the starting point in these researches is 4-*nitroaceto-o-toluidide* (X), it follows that the entrant nitro-group must be in position 3 or 5. The latter position is excluded because of the simultaneous formation of the isomeric 3 : 4- and 4 : 5-dinitro-aceto-*o*-toluidides (I and XI) (Brady and Williams, *loc. cit.*). The
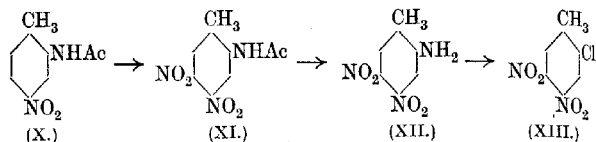
latter acetyl-4 : 5-dinitro-derivative, on hydrolysis, gives 4 : 5-dinitro-*o*-toluidine (XII), which has now (p. 1703) been converted into 2-chloro-4 : 5-dinitrotoluene (XIII). Since the other dinitro-*o*-toluidine (II) derived from 4-nitroaceto-*o*-toluidide (X) leads to an *ortho*-diamine (VIII), it follows that the entrant nitro-group is in position 3. The constitution of the new 2-chloro-3 : 4-dinitro-toluene is therefore completely demonstrated.

EXPERIMENTAL.

The nitration of 4-nitroaceto-*o*-toluidide was carried out by the method described by Brady and Williams (*loc. cit.*), and the mixture of 3 : 4-dinitro- and 4 : 5-dinitro-aceto-*o*-toluidides was hydrolysed and separated as follows. Ninety-two grams of the mixture were heated for six hours on the water-bath with 360 c.c. of concentrated sulphuric acid diluted with 720 c.c. of water. The precipitate (42 grams) which had separated on cooling was washed successively with 50 per cent. sulphuric acid and with water; it was then crystallised twice from absolute alcohol and twice from 50 per cent. alcohol, when purified 3 : 4-dinitro-*o*-toluidine (32 grams) was obtained, melting at 130°.

The acid filtrate from the crude 3 : 4-dinitro-compound, when diluted with water, furnished 17 grams of crude 4 : 5-dinitro-*o*-toluidine, which, after repeated crystallisation from alcohol, melted at 190°, the yield of purified base being 13 grams. 3 : 4-*Dinitro-aceto-o-toluidide* was prepared by adding a drop of concentrated sulphuric acid to 1 gram of 3 : 4-dinitro-*o*-toluidine in 3 c.c. of acetic anhydride; the base dissolved with considerable generation of heat and the greater part of the acetyl derivative crystallised out immediately. Water was then added and the product crystallised repeatedly from dilute acetic acid, when it separated in brittle, yellowish-white needles melting at 186° (Found : N = 17·73.

$C_9H_9O_5N_3$ requires $N = 17.57$ per cent.). 4 : 5-*Dinitroaceto*-o-*toluidide*, prepared and purified as in the preceding preparation, was obtained in colourless needles melting at 180° (Found : $N = 17.80$ per cent.).

2-*Chloro*-3 : 4-*dinitrotoluene* (III).

Twenty grams of 3 : 4-dinitro-o-toluidine, 50 c.c. of concentrated hydrochloric acid, and 300 c.c. of absolute alcohol were heated on the water-bath for thirty minutes and treated with 100 c.c. of 10 per cent. cuprous chloride, prepared by reducing with copper 10 grams of copper carbonate in 100 c.c. of concentrated hydro-chloric acid. To the warm solution at 70°, 30 grams of sodium nitrite in 100 c.c. of water were slowly added from a tap-funnel dipping below the surface of the liquid. The alcohol was evaporated and the residual oil allowed to solidify over-night to a brown mass, which was washed with water, dissolved in absolute alcohol, and the solution taken to dryness on the water-bath. The dried residue was extracted three times with 60 c.c. of boiling petroleum (b. p. 80°). This extract was concentrated to 20 c.c., when an oil separated which solidified on cooling. The product, after draining on porous tile, was dissolved in 50 c.c. of boiling glacial acetic acid, the solution cooled to 60°, and diluted with water until cloudy. The solid which separated on cooling was repeatedly submitted to this process with acetic acid and water until pure 2-chloro-3 : 4-dinitrotoluene was obtained. The filtrates at each stage of the process were diluted further with water to obtain additional crops of the product.

2-*Chloro*-3 : 4-*dinitrotoluene*, obtained by this process of purifica-tion, separated in colourless needles melting at 89°; a mixed melting point with an equal weight of 2-chloro-4 : 5-dinitrotoluene (m. p. 88.5°) gave 55° (Found : $N = 13.28$, 13.14; $Cl = 16.58$. $C_7H_5O_4N_2Cl$ requires $N = 12.93$; $Cl = 16.37$ per cent.).

2-Chloro-3 : 4-dinitrotoluene dissolved readily in acetone, benzene, chloroform, or acetic acid, but was more sparingly soluble in petroleum. The following colour changes were observed : with warm aqueous sodium hydroxide, yellow (transparent), yellowish-brown (tr.), brownish-red (tr.); with alcoholic sodium hydroxide, pale green (tr.), dark green (tr.), greenish-black (opaque), brownish-black (op.) and after heating and leaving for two hours, pale red (tr.); with alcoholic ammonia, faint yellow (tr.).

2-*Chloro*-4 : 5-*dinitrotoluene from* 4 : 5-*Dinitro-o-toluidine*.

The foregoing experiment was repeated on 4 : 5-dinitro-o-toluidine; the crude chloro-compound was extracted successively with alcohol,

petroleum (b. p. 80°), and dilute acetic acid. Repeated crystallisation from the last of these solvents yielded 2-chloro-4 : 5-dinitrotoluene in colourless needles melting at 87°. This product was identified by a mixed melting point with a specimen obtained by nitrating 2-chloro-4-nitrotoluene.

Reactions of 2-Chloro-3 : 4-dinitrotoluene with Bases.

(1) *2-Chloro-4-nitro-m-toluidine* (VI).—2-Chloro-3 : 4-dinitrotoluene was dissolved and left for fourteen days in about sixty parts of absolute alcohol saturated with ammonia. The solution acquired a yellow colour, and on dilution with an equal bulk of water gave a yellow solid which, after two crystallisations from dilute alcohol, separated in lustrous, golden-yellow needles melting at 105°; the yield was quantitative (Found : $N = 14.94$. $C_7H_7O_2N_2Cl$ requires $N = 15.02$ per cent.).

2-Chloro-4-nitro-m-toluidine was readily soluble in alcohol, acetone, chloroform, or benzene, but dissolved less readily in light petroleum. With alcoholic sodium hydroxide, it gave a deep orange-red coloration.

The substitution of the amino-group for the 3-nitro-radicle in 2-chloro-3 : 4-dinitrotoluene was demonstrated in the following manner : 2-Chloro-4-nitro-m-toluidine (0·4 gram) was dissolved in a mixture of 7 c.c. of concentrated sulphuric acid and 3 c.c. of water; 0·4 gram of powdered sodium nitrite was added slowly to the mixture cooled to −5°. Small fragments of ice were then gradually introduced, the nitrite dissolved, and when 20 grams of ice were added the diazotisation was complete. The solution was then added to 20 c.c. of boiling alcohol and the mixture boiled for a few minutes. The alcohol was evaporated and the residue distilled in steam. The oily distillate solidified, and was identified as 2-chloro-4-nitrotoluene by a mixed melting point with a standard specimen (m. p. 65°). The alcoholic distillate and the residue in the distilling-flask gave further quantities of 2-chloro-4-nitrotoluene, the total yield being 70 per cent.

(2) *2-Chloro-4-nitro-N-phenyl-m-toluidine* (IV).—2-Chloro-3 : 4-dinitrotoluene (0·75 gram) and 2 c.c. of aniline were dissolved in 50 c.c. of absolute alcohol and boiled under reflux for twenty hours. The solution became successively yellow and dark red, while a tarry product separated. Water and dilute hydrochloric acid were then added, the excess of aniline was dissolved, and the solid residue, which acquired a pink colour, crystallised in succession from alcohol and petroleum (b. p. 80°); the latter solvent did not dissolve the tar. The orange-red residue from the petroleum extract was

crystallised repeatedly from dilute alcohol, when it separated in orange-red needles melting at 95° (Found: $N = 10.78$. $C_{13}H_{11}O_2N_2Cl$ requires $N = 10.67$ per cent.).

2-Chloro-4-nitro-N-phenyl-m-toluidine was readily soluble in acetone, chloroform, benzene, or alcohol, but less soluble in light petroleum. In hot concentrated sulphuric acid, this base developed successively violet, purplish-red, deep red, and, finally, brownish-black colorations. The orientation of the phenylamino-group in the preceding base was demonstrated as follows :

2-Chloro-4-nitro-m-toluidine (0·2 gram), 1 c.c. of bromobenzene, 0·1 gram of anhydrous potassium carbonate, and a trace of cuprous iodide in 10 c.c. of nitrobenzene were boiled under reflux for twenty hours. The dark reddish-brown solution was distilled in steam to remove nitrobenzene and excess of bromobenzene, and the residual oil dissolved in absolute alcohol. The alcoholic extract was evaporated to dryness and the residue extracted repeatedly with hot petroleum (b. p. 80°). This extract was also evaporated to dryness and the residue crystallised repeatedly from dilute alcohol, when orange-yellow needles were obtained melting at 89°. This melting point was not depressed by mixing the product with the pure 2-chloro-4-nitro-N-phenyl-m-toluidine (m. p. 95°). Hence the two preparations give rise to identical substances and the orientation of the N-phenylamino-group in position 3 is confirmed.

2-Chloro-3 : 4-dinitrotoluene did not condense with m-nitro-aniline to give a substituted tolylphenylamine derivative, in this respect differing from 2 : 3 : 4-trinitrotoluene, which condenses with m-nitroaniline on prolonged heating (*Proc. Roy. Irish Acad.*, 1918, **31**, 103).

(3) 4-*Chloro*-1-*hydroxy*-5-*methyl*-1 : 2 : 3-*benzotriazole* (V).—Hydrazine hydrate (0·5 c.c. of 50 per cent. solution) dissolved in 1·5 c.c. of absolute alcohol was added to 0·5 gram of 2-chloro-3 : 4-dinitro-toluene in 4 c.c. of boiling alcohol. The solution reddened, a vigorous reaction set in lasting about a minute, and the liquid became yellow. On cooling, the mixture became semi-solid from the separation of a colourless, crystalline product, which, after recrystallisation from absolute alcohol, separated in colourless needles decomposing somewhat indefinitely at 218—225° (Found : $N = 32.61$. The *hydrazine* salt, $C_7H_6ON_3Cl,N_2H_4$, of the hydroxy-triazole requires $N = 32.49$ per cent.).

The concentrated aqueous solution of this hydrazine salt was acidified with hydrochloric acid, when the hydroxytriazole separated. It crystallised from dilute alcohol in colourless, hexagonal plates darkening at 208° and melting with vigorous decomposition at

210—212° (Found : N = 22·95. $C_7H_6ON_3Cl$ requires N = 22·88 per cent.).

This hydroxytriazole was sparingly soluble in cold water, but dissolved readily in alcohol; its hydrazine salt was very soluble in cold water, and sparingly soluble in cold alcohol; it deflagrated on heating.

2-Chloro-3 : 4-tolylenediamine (VIII).

Zinc dust (0·5 gram) and 0·4 gram of ammonium chloride were added to 0·8 gram of 2-chloro-4-nitro-m-toluidine in 12 c.c. of alcohol and 4 c.c. of water.   The mixture was refluxed for thirty minutes, another 0·5 gram of zinc dust was added, and the heating continued for a further thirty minutes, when the greenish-brown liquid had become colourless.   The zinc dust was quickly filtered and the filtrate cooled in a freezing mixture and saturated with hydrogen chloride.   The precipitated hydrochloride was dissolved in cold, strong, aqueous sodium hydroxide, when the free diamine separated as a light brown oil which quickly solidified.   Repeated crystallisation from petroleum (b. p. 80°) yielded the diamine in pale brown needles melting at 55—56° (Found : N = 17·92. $C_7H_9N_2Cl$ requires N = 17·89 per cent.).

2-Chloro-3 : 4-tolylenediamine was very soluble in the ordinary organic media excepting light petroleum; it was readily oxidised when its alcoholic solution was exposed to air.

5-Chloro-2 : 3-diphenyl-6-methylquinoxaline (IX).

One gram of 2-chloro-4-nitro-m-toluidine was reduced to 2-chloro-3 : 4-tolylenediamine and the crude diamine added to 1 gram of benzil in 10 c.c. of warm alcohol, the mixture being refluxed for one and a half hours.   On cooling the yellow solution, the quinoxaline separated as a pale yellow solid which, after two crystallisations from alcohol, was obtained in clusters of yellowish-white needles melting at 143° (Found : N = 8·69. $C_{21}H_{15}N_2Cl$ requires N = 8·47 per cent.).   This quinoxaline developed a red coloration with cold concentrated sulphuric acid.

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CXCV.—*Dinaphtha*-1 : 7 : 1′ : 7′-*diquinone.*

By GILBERT T. MORGAN and DUDLEY CLOETE VINING.

ALTHOUGH at least six naphthaquinones are theoretically possible, only three have so far been isolated, namely, α- or 1 : 4-naphthaquinone, β- or 1 : 2-naphthaquinone, and *amphi-* or 2 : 6-naphthaquinone, all of which can be obtained by the oxidation of the corresponding dihydroxynaphthalenes. The *peri-* or 1 : 8-naphthaquinone of Meldola and Hughes was subsequently shown by Liebermann and Schlossberg to be 2 : 2′-dinaphtha-1 : 4 : 1′ : 4′-diquinone (T., 1890, **57**, 393, 631; *Ber.*, 1899, **32**, 546, 868), and there is at present little evidence for the existence of derivatives of the 1 : 8-quinone (compare Quincke, *Ber.*, 1888, **21**, 1460). Derivatives of 2 : 3-naphthaquinone have been described, for example, 4 - chloro - 6 - bromo - 1 - methyl - 2 : 3 - naphthaquinone (Fries and Empson, *Ber.*, 1909, **42**, 3375).

In addition to the three naphthaquinones there are known to be two diquinones containing dinaphthyl residues, namely, 1 : 1′-dinaphtha-3 : 4 : 3′ : 4′-diquinone (Stenhouse and Groves, *Annalen*, 1878, **194**, 205; T., 1878, **33**, 415; Zincke and Rathgen, *Ber.*, 1886, **19**, 2483) and 2 : 2′-dinaphtha-1 : 4 : 1′ : 4′-diquinone (Staub and Smith, T., 1885, **47**, 104; Chattaway, *ibid.*, 1895, **67**, 657; Witt and Dedichen, *Ber.*, 1897, **30**, 2663; Liebermann and Schlossberg, *loc. cit.*; Meldola and Hughes, *loc. cit.*). These diquinones are produced by oxidising various compounds containing only one naphthalene nucleus and indicate a tendency for two naphthyl residues to coalesce during oxidation.

In 1907, Willstätter and Parnas succeeded in obtaining 2 : 6-naphthaquinone by the oxidation of 2 : 6-dihydroxynaphthalene in hot anhydrous benzene with excess of lead peroxide (*Ber.*, 1907, **40**, 1406), but their paper contains no indication as to whether or not they extended their investigation to other dihydroxynaphthalenes which might be expected to furnish the remaining, theoretically possible naphthaquinones.*

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* Since this paper was communicated to the Society, Professor Barger has kindly lent me (G.T.M.) a copy of the dissertation by Parnas (Munich, 1908), from which it appears that oxidation experiments were made on 1 : 7-, 1 : 8-, and 1 : 5-dihydroxynaphthalenes. In the case of the first of these the thesis states:

"Bleisuperoxyd wirkt nicht ein; es wurde bei Oxydationsversuchen damit immer nur wenig unreines Ausgangmaterial zurückgewonnen; nichts liefs auf die Bildung eines Chinons schliefsen."

There is also a reference to a transient violet coloration produced by silver oxide on the 1 : 7-isomeride in ethereal solution.

3 N*

The experiments recorded in the present research were carried out on 1 : 7-dihydroxynaphthalene (I), which on oxidation should yield by a rearrangement of single and double linkings the unknown 1 : 7-naphthaquinone (II)
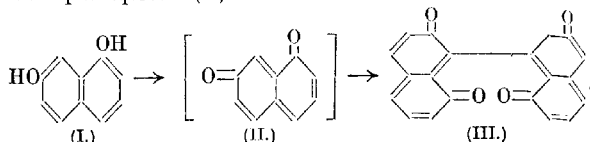
In this case, however, oxidation proceeded a stage further, and the product obtained in a yield of about 5 per cent. proved to be a new diquinone, *dinaphtha*-1 : 7 : 1' : 7'-*diquinone*, where the numbering refers to the original orientation of the quinonoid oxygen atoms. It has not been found possible to determine with certainty the positions at which the condensation of the two naphthalene nuclei has occurred, although the steric hindrance noticeable in the formation of *dinaphtha*-1 : 7 : 1' : 7'-*diquinone-dioxime*, $C_{20}H_{10}O_2(NOH)_2$, suggests a grouping together of the ketonic radicles as shown in formula III. Structural formula IV is not, however, altogether excluded, but the configuration V is rendered very improbable by the fact that the diquinone was not
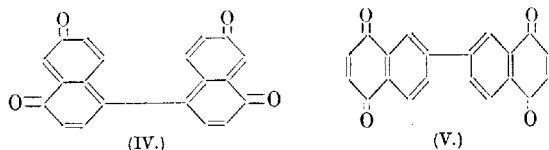
obtained by the oxidation of 1 : 6-dihydroxynaphthalene. If the diquinone is derived from a condensation of 6- or 7-hydroxy-1 : 4-naphthaquinone, then both 1 : 6- and 1 : 7-dihydroxynaphthalenes should yield it.

Dinaphtha-1 : 7 : 1' : 7'-diquinone forms a well-defined, yellow benzene additive compound, $C_{20}H_{10}O_4,C_6H_6$; the combined hydrocarbon is eliminated on exposure to the atmosphere or more rapidly on warming. The benzene-free diquinone is obtained in pale orange crystals which are thermotropic, becoming bright red on heating to 160°. This colour change is reversed on cooling.

Owing to the small yield of dinaphtha-1 : 7 : 1' : 7'-diquinone obtainable from 1 : 7-dihydroxynaphthalene the total amount of this oxidation product at our disposal for the following experiments did not exceed 3·5 grams, and on this account the constitution of the diquinone was not completely demonstrated. But preliminary

investigations showed that two promising lines of research are suggested by a study of the reduction products of the diquinone.

$1 : 7 : 1′ : 7′$-*Tetrahydroxydinaphthyl*, $C_{20}H_{10}(OH)_4$, is produced almost quantitatively by reducing the diquinone with amalgamated aluminium or hydriodic acid. The diquinone is not reduced by sulphurous acid, but distillation with zinc dust leads to the formation of an extremely stable, volatile substance subliming and crystallising in yellow needles; this product is probably a quinonoid compound arising from the partial deoxidation of the diquinone.

<div align="center">EXPERIMENTAL.</div>

$1 : 7$-*Dihydroxynaphthalene* (Emmert, *Annalen*, 1887, **241**, 371).— The crocein salt (sodium β-naphthol-8-sulphonate) employed as the starting material in these experiments was presented to us by the British Dyestuffs Corporation, to whom and to Mr. J. Baddiley of this firm our best thanks are tendered. Four hundred grams of 64 per cent. crocein salt were added during thirty minutes to 1,200 grams of fused potassium hydroxide at 230—240°. The temperature was then raised to 250° and maintained at 245—255° for thirty minutes, the fused mass being thoroughly stirred. The cooled fusion, broken into small pieces, was dissolved in 2,800 c.c. of water and acidified with 1,840 c.c. of concentrated hydrochloric acid. The tar was separated and extracted in a Soxhlet apparatus with chloroform. The aqueous solution on cooling yielded 1 : 7-dihydroxynaphthalene, and more of this product was obtained by extraction with chloroform. The yield of 1 : 7-dihydroxynaphthalene from tar and aqueous liquors was upwards of 40 per cent. of the theoretical amount. When purified by repeated crystallisation from benzene, 1 : 7-dihydroxynaphthalene was obtained in almost colourless needles melting at 178°.

Lead Dioxide.—A rapid stream of chlorine was passed into a well stirred, aqueous solution (900 c.c.) of lead acetate (190 grams) and sodium hydroxide (100 grams). The chocolate-brown lead dioxide was collected, washed, dried, finely powdered and again dried to constant weight at 120°. This preparation was very active, and ignition accompanied by slight explosions occurred on rubbing the dioxide in contact with organic materials.

Purified Benzene.—Good commercial benzene was treated successively with sulphuric acid, chromic acid mixture, sodium hydroxide, and water. It was then dried over calcium chloride, refluxed over sodium for two hours, and finally distilled fractionally from this metal. These precautions were proved to be necessary, for when 1 : 7-dihydroxynaphthalene was oxidised in benzene

<div align="center">3 N* 2</div>

containing toluene an appreciable amount of benzoic acid was isolated. This impurity did not appear in benzene freed from toluene.

Oxidation of Dihydroxynaphthalenes with Metallic Peroxides.

The experiments of Willstätter and Parnas were repeated, 200 grams of lead dioxide being used to oxidise 3 grams of 2 : 6-dihydroxynaphthalene, when yields of *amphi*(2 : 6-)naphthaquinone were obtained varying from 10 to 20 per cent. of the calculated amount. On replacing lead dioxide by nickelic oxide, the yield was diminished, and a negative result was obtained on employing the following oxidising mixture (CuO, 1 part; MnO_2, 6 parts; Co_2O_3, 3 parts; Ag_2O, 1 part).

1 : 6-Dihydroxynaphthalene was treated in cold dry benzene with lead dioxide, as described below for the 1 : 7-isomeride. The benzene filtrate was colourless and gave no residue on evaporation; there was no indication of quinone formation, and no unchanged dihydroxynaphthalene could be recovered. The oxidation had evidently taken a different course from that manifested in the following experiment.

Oxidation of 1 : 7-Dihydroxynaphthalene.—Preliminary experiments showed that oxidation with lead dioxide in boiling benzene (Willstätter and Parnas, *loc. cit.*) was too violent, the yield of diquinone being only 0·5 to 1 per cent. A more favourable result was obtained as follows : Five grams of finely powdered 1 : 7-dihydroxynaphthalene were added all at once to 125 grams of freshly-prepared, well-dried lead dioxide suspended in pure dry benzene (400 c.c.) at the ordinary temperature; the mixture was shaken continuously for five minutes, when the temperature rose about 5°. The lead dioxide was collected rapidly, drained and returned to the reaction vessel with 100 c.c. of fresh benzene; the mixture was shaken for a further five minutes and filtered rapidly. The united filtrates, which were intensely yellow, were distilled under 20—30 mm. pressure to about 50 c.c., when the diquinone-benzene compound separated in well-defined, transparent, lemon-yellow, flat, elongated four-sided prisms with oblique ends. A further crop was obtained on the addition of petroleum (b. p. 40—60°); the highest yield obtained was 5·3 per cent.

An air-dried specimen of the additive compound, when heated at 100° in a vacuum to constant weight, lost 20·26 per cent. $C_{20}H_{10}O_4,C_6H_6$ requires $C_6H_6 = 19\cdot90$ per cent. The orange, benzene-free diquinone gave C = 76·44; H = 3·71. $C_{20}H_{10}O_4$ requires C = 76·42; H = 3·21 per cent.

Molecular Weight Determinations.—Ebullioscopic method in

benzene : $w/W = 1\cdot10/100$, $\Delta t = 0\cdot085°$, whence $M = 340$; in acetone, $w/W = 2\cdot97/100$, $\Delta t = 0\cdot176°$, whence $M = 289$.

Microscopic method (Barger, T., 1904, **85**, 286), using acetone as solvent and benzil as standard substance. Comparable determinations were made with two of the simple naphthaquinones.

α-(1 : 4)-Naphthaquinone, $M = 159$.   Dinaphtha-1 : 7 : 1' : 7'-diquinone,
β-(1 : 2)-Naphthaquinone, $M = 171$. $M = 279$.
    $C_{10}H_6O_2$ requires $M = 158$. $C_{20}H_{10}O_4$ requires $M = 314$.

Dinaphtha-1 : 7 : 1' : 7'-*diquinone* crystallised from solvents other than benzene in pale orange, square tablets; on heating, it commenced to darken at 110°, and was bright red at 160°. At 214°, it became brown, and melted with decomposition at 217°. On cooling from 160°, the diquinone reverted to the pale orange form. When moistened with benzene or when exposed to the vapour of this hydrocarbon, it became yellow, owing to the formation of the benzene additive compound. The resulting lemon-yellow crystals on exposure to air lost their transparency, and darkened in colour owing to partial loss of benzene; this elimination was completed after six days in a vacuum over paraffin wax. At 100° in a vacuum, the benzene was removed in fifteen minutes.

The diquinone, which was inodorous and non-volatile, dissolved only sparingly in ether, alcohol, acetic acid, ethyl acetate, carbon tetrachloride, carbon disulphide, or chlorobenzene, but was slightly more soluble in benzene (1 in 250 at 20°, 1 in 100 at 80°) or chloroform, and appreciably more so in acetone. With an alcoholic solution of guaiacum resin it developed a blue coloration; with concentrated sulphuric acid a brown, insoluble substance separated. In nitric acid, it became bright red, dissolving to an orange solution, from which a reddish-brown precipitate was deposited on dilution.

In view of the small yield of diquinone, search was made for other products of the oxidation of 1 : 7-dihydroxynaphthalene. The benzene extract contained no other substance; the lead oxide residues gave no organic material on extraction with the ordinary solvents, but on treatment with organic or mineral acids a considerable amount of carbon dioxide was evolved, indicating complete oxidation of dihydroxynaphthalene to a carbonate. The acid liquor was yellow, and on extraction with ether or chloroform yielded a small amount of gummy residue smelling of benzoquinone and of a higher fatty acid. These results also pointed to far-reaching oxidation.

Dinaphtha-1 : 7 : 1' : 7'-*diquinonedioxime*, $C_{20}H_{10}O_2(NOH)_2$.

Hydroxylamine sulphate (0·35 gram) and potassium hydroxide (0·5 c.c. of 50 per cent. solution) were added in the cold to the

benzene-free diquinone (0·25 gram) in 12 c.c. of alcohol. The solution, which reddened immediately, was heated on the water-bath for three hours, cooled, filtered, and concentrated at the ordinary temperature in a vacuum. The dark red, scaly residue, when dissolved in alcohol, yielded on addition of water a red, crystalline powder, which crystallised from aqueous alcohol in brownish-red flakes having no melting point below 300° (Found : $N = 8·00$. $C_{20}H_{12}O_4N_2$ requires $N = 8·13$ per cent.). Although more than sufficient hydroxylamine was used to give a tetraoxime, only the dioxime was actually obtained (yield 50 per cent.).

Dinaphtha-1 : 7 : 1′ : 7′-*diquinonetetra*-2 : 4-*dinitrophenylhydrazone*, $C_{20}H_{10}[N·NH·C_6H_3(NO_2)_2]_4$.

The diquinone (0·2 gram) dissolved in 12 c.c. of hot glacial acetic acid containing 0·52 gram of 2 : 4-dinitrophenylhydrazine to a dark red solution, which after one hour was diluted with water, when a dark purple-brown powder was precipitated. The yellow mother-liquor was concentrated in a vacuum desiccator over soda-lime until a yellow, crystalline powder separated. Recrystallised from aqueous alcohol, this tetrahydrazone appeared in golden-yellow needles melting and decomposing at 193—194°, the yield being about 20 per cent. (Found : $N = 22·05$. $C_{44}H_{26}O_{16}N_{16}$ requires $N = 21·67$ per cent.).

The less soluble, purple product (yield about 20 per cent.) was probably a dihydrazone; it separated from aqueous alcohol as a purple-brown, lustrous powder decomposing at 205—206°, but it could not be obtained definitely crystalline.

Attempts to isolate the anilide of the diquinone failed on account of the uncrystallisable nature of the products.

Reduction of Dinaphtha-1 : 7 : 1′ : 7′-*diquinone :* 1 : 7 : 1′ : 7′-*Tetrahydroxydinaphthyl*, $C_{20}H_{10}(OH)_4$.

Freshly-prepared, moist amalgamated aluminium (made from aluminium wire) was added in portions of 2 grams to a solution of the diquinone (0·5 gram) in 50 c.c. of moist ether and 25 c.c. of acetone in a reflux apparatus. After two hours, when the originally yellow solution had become colourless, the filtered liquid was washed with a little water, dried over calcium chloride, and distilled to dryness under 100 mm. pressure, the drying being finally completed in a vacuum desiccator. The oily residue solidified to a pale yellow, semi-crystalline mass, which was dried on porous tile and washed with a little benzene to remove a brown impurity. The

tetrahydroxydinaphthyl, thus obtained in almost theoretical yield, was crystallised from hot benzene or benzene-petroleum (b. p. 80—100°) in hard, yellowish-white, nodular crystals or from ether or acetone in small, slightly yellow, acicular prisms melting at 215—216° (Found : C = 75·80; H = 5·44. $C_{20}H_{14}O_4$ requires C = 75·45; H = 4·43 per cent.).

1 : 7 : 1' : 7'-*Tetrahydroxydinaphthyl* was readily soluble in alcohol, ether, or acetone. Unlike the diquinone, it showed no tendency to retain benzene of crystallisation. It gave no coloration with ferric chloride, and its solution in aqueous sodium hydroxide rapidly became reddish-purple on exposure to air.

The *tetra-acetyl* derivative, $C_{20}H_{10}(O \cdot CO \cdot CH_3)_4$, was obtained in quantitative yield by heating 1 : 7 : 1' : 7'-tetrahydroxydinaphthyl with excess of acetic anhydride and anhydrous sodium acetate on the water-bath for one and a half hours; the solution was then evaporated to dryness in a vacuum desiccator, the residue washed with water, and the insoluble portion crystallised from benzene-petroleum, from which the compound separated in small, flattened, yellowish-white prisms melting at 188—189° (Found : C = 69·00; H = 5·11. $C_{28}H_{22}O_8$ requires C = 69·12; H = 4·56 per cent.).

The tetra-acetate was readily soluble in benzene, but less so in alcohol.

Reduction of Dinaphtha-1 : 7 : 1' : 7'-diquinone with Hydriodic Acid.

Twenty c.c. of 10 per cent. potassium iodide solution and 20 c.c. of dilute sulphuric acid (1 in 4 vols.) were added to an alcoholic solution (20 c.c.) of the diquinone (0·1109 gram). Iodine was liberated forthwith and titrated with $N/10$-sodium thiosulphate and starch-paper indicator, when 84·6 per cent. of the calculated amount was determined. The resulting solution was treated with excess of sodium acetate, concentrated under reduced pressure to half its bulk, and filtered from a green, flocculent material (quinhydrone ?) not melting below 300°. The ethereal extract of the filtrate furnished tetrahydroxydinaphthyl (yield 73 per cent.). Willstätter and Parnas found that with 2 : 6-naphthaquinone and hydriodic acid the iodine liberated and the 2 : 6-dihydroxynaphthalene produced were respectively 76 and 25 per cent. of the calculated amounts.

Reduction of the Diquinone with Heated Zinc Dust.

The diquinone (0·4 gram) mixed with 3 grams of zinc dust was distilled in a hard-glass tube through a layer of 10 grams of zinc

dust, when an intensely yellow substance sublimed on to the cool part of the tube, accompanied by traces of naphthalene. The coloured product was odourless and sparingly soluble in ether or acetone to faintly blue fluorescent solutions. From these solvents it was obtained in minute, yellow needles melting at 238—239°. This substance, which still retained quinonoid characters, sublimed with difficulty and was very stable at temperatures above its melting point. On further heating with zinc dust, naphthalene was produced, but much of the substance sublimed unchanged. It was insoluble in aqueous sodium hydroxide, and gave a purple coloration with nitric acid. Lack of material has prevented a complete examination of this interesting product, the reactions of which would probably throw further light on the constitution of the diquinone.

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CXCVI.—*Chenopodium Oil.*

By THOMAS ANDERSON HENRY and HUMPHREY PAGET.

THE oil distilled from *Chenopodium ambrosioides* var. *anthelminticum* is now being used on a considerable scale in the campaigns against hookworm disease that are being carried on in various parts of the Tropics under the auspices of the International Health Board of the Rockefeller Foundation.

As a result of the investigations conducted by Kremers (*Pharm. Rev.*, 1907, **25**, 155), Schimmel & Co. (Bericht von Schimmel & Co., April, 1908, p. 109), and Nelson (*J. Amer. Chem. Soc.*, 1911, **33**, 1404; 1913, **35**, 84; 1914, **36**, 2521), it is known that the oil consists chiefly of a liquid organic peroxide, ascaridole, $C_{10}H_{16}O_2$, and a mixture of liquid hydrocarbons, of which until last year only one, cymene, had been identified with certainty. To account for the optical activity and a characteristic colour reaction of the hydrocarbon fraction, Schimmel & Co. suggested the presence of sylvestrene (*loc. cit.*), but this has received no support from later

investigators (compare Wirth, *J. Amer. Pharm. Assoc.*, 1920, **9**, 139). Since the present authors began their work Nelson has re-examined the hydrocarbon fraction and produced evidence of the presence of α-terpinene and *l*-limonene (*J. Amer. Chem. Soc.*, 1920, **42**, 1204), whilst Caius and Mhaskar have stated, without adducing any experimental data, that the fraction contains cymene, terpinene, and phellandrene (*Ind. J. Med. Res.*, 1920, **7**, 570).

It has been assumed generally that the value of the oil as an anthelmintic is due to the ascaridole, but Hall and Hamilton have asserted as a result of an extensive series of pharmacological trials that the " lighter " portions (that is, the hydrocarbon fraction) are more active as anthelmintics than the " heavier " (ascaridole) fractions (*J. Pharm. Exp. Ther.*, 1918, **11**, 89). In view of this confusion, it seemed to the authors desirable that the oil should be re-examined and the nature and pharmacological action of its components definitely settled.

The pharmacological examination of the substances isolated from the oil has been undertaken by Dr. Wilson G. Smillie of the Instituto de Hygiene, San Paulo, Brazil, who has already obtained a number of interesting results, which will be recorded elsewhere.

EXPERIMENTAL.

Six lots of chenopodium oil, purchased through ordinary trade channels, were used. These had the following constants :

	(1)	(2)	(3)	(4)	(5)	(6)
d_{15}^{15}	0·9665	0·9663	0·9712	0·9723	0·9672	0·9582
Sp. rotation $[\alpha]_D^{15}$	$-5\cdot7°$	$-4\cdot5°$	$-5\cdot3°$	$-5\cdot3°$	$-6\cdot3°$	$-6\cdot8°$

The oils were separated by distillation under 15 mm. pressure into three fractions: (*a*) b. p. below 84°, d_{15}^{15} 0·8596 to 0·8839, $[\alpha]_D^{15}$ $-14°$ to $-18°$; (*b*) b. p. 84—104°, d_{15}^{15} 0·9200 to 1·0070, $[\alpha]_D^{15}$ $-5°$ to $-11°$; and (*c*) b. p. 104—118°, d_{15}^{15} 1·0120 to 1·0160, $[\alpha]_D^{15}$ $-0\cdot25°$ to $-1\cdot18°$, which usually formed about 25, 15, and 55 per cent. respectively of the whole oil. The residual 5 per cent. is chiefly ascaridole glycol. The oil is difficult to fractionate, especially in the later stages, owing to the risk of explosive decomposition of the ascaridole. Fraction (*a*) consisted mainly of hydrocarbons, (*b*) of a mixture of hydrocarbons and ascaridole, and (*c*) was almost pure ascaridole. Fraction (*b*) was further treated by carefully heating it under a reflux condenser at atmospheric pressure, when the ascaridole decomposed with considerable violence, but without loss, giving the isomeric ascaridole glycol anhydride. On steam-distilling the product, the anhydride yielded the corresponding glycol, which was not volatile in steam, so that the distillate

consisted almost wholly of hydrocarbons; this was added to fraction (a), which then formed about 30 per cent. of the whole oil.

Examination of the Hydrocarbon Fraction.

Acids.—On repeated agitation with 5 per cent. solution of sodium carbonate, the fraction yielded 0·9 per cent. of oily material having the characteristic odour of the lower fatty acids. This was converted into silver salts by neutralisation and precipitation in three portions with silver nitrate (Found : Ag = 56·27, 55·8, 57·6. Silver butyrate, $C_4H_7O_2Ag$, requires Ag = 55·4 per cent.).

Methyl Salicylate.—On further agitation of the fraction with 4 per cent. solution of sodium hydroxide, there was obtained on acidification 1·5 per cent. of a red oil, which on standing solidified in part, owing to the separation of salicylic acid (m. p. 156°), and the rest of the acid was removed by shaking the liquid portion with sodium carbonate solution. The liquid portion then boiled at 220°/755 mm., gave a benzoyl derivative, m. p. 83°, and was there-fore methyl salicylate; the salicylic acid is no doubt formed by the action of the alkali on the ester during extraction.

As no evidence of the presence of other oxygenated compounds could be obtained, the mixture was then redistilled several times through a six-bulb Young dephlegmator, which separated it into three fractions boiling at 166—173°, 174—177°, and 177—180° under 765 mm. pressure. The middle fraction formed the bulk of the mixture, and this, on redistillation, was found to consist of a product having the following constants : b. p. 176·5—177°/765 mm.; $d_{15°}^{29°}$ 0·8491; $[\alpha]_D^{20}$ −18·09°; n_D^{20} 1·48320. It had a slight lemon-like odour, and its solution in acetic anhydride gave a transient, bluish-red coloration with sulphuric acid. This product was pre-pared without difficulty from all six oils, and in spite of its constant boiling point was subsequently found to be a mixture of at least three hydrocarbons. The results of the analysis (Found : C = 88·14, 88·16, 88·63; H = 11·40, 11·10, 11·21) agree fairly well with those required for a mixture of terpenes, $C_{10}H_{16}$, with cymene, $C_{10}H_{14}$, in about equal proportions (namely, C = 88·9; H = 11·08 per cent.), and further evidence was obtained later of the presence of approxi-mately this quantity of cymene.

Attempts to effect a further separation by distillation at different pressures through a twelve-bulb Young dephlegmator were unsuccessful.

Identification and Removal of α-Terpinene.—Further separation of the mixture by physical means having failed, recourse was had to the identification of the components and attempts to eliminate

these in succession. On treatment with sodium nitrite in presence of acetic acid at 0°, the mixture gave a nitrosite, which, after recrystallisation from ethyl acetate, had m. p. 155° and showed no depression of melting point on admixture with α-terpinene nitrosite made from terpinene, prepared from either turpentine oil or terpineol. The formation of α-terpinene nitrosite had already been recorded by Nelson (loc. cit. Compare Caius and Mhaskar, loc. cit.), who, however, failed to obtain any other evidence of the presence of α-terpinene. Caius and Mhaskar state that phellandrene is also present. Phellandrene gives even in small quantities an excellent yield of a nitrosite of unmistakable appearance, and the present authors were unable to find any evidence of the formation of phellandrene nitrosite along with the α-terpinene derivative in the reaction.

Baeyer has shown (Ber., 1894, **27**, 815) that small quantities of terpinene can be removed from its mixtures with other terpenes by repeated agitation in the cold with Beckmann's chromic acid mixture. Two hundred c.c. of the hydrocarbon fraction were treated repeatedly with small quantities of chromic acid mixture until no further absorption, and no increase in the specific rotation of the recovered oil, took place. The recovered oil, after distillation over sodium, had b. p. 176·5—177°/758 mm., d^{23} 0·8545, $[\alpha]_D^{15}$ −23·08°, n_D^{20} 1·48637 (Found : C = 89·08, 88·92, 88·80; H = 10·86, 10·59, 10·65. A mixture of terpene, $C_{10}H_{16}$, with cymene, $C_{10}H_{14}$, in the proportion of about 40 : 60 requires C = 89·04; H = 10·96 per cent.).

The recovered oil gave no crystalline nitrosite on treatment with sodium nitrite in acetic acid at 0°, but still gave the characteristic bluish-red coloration with sulphuric acid in presence of acetic anhydride, and on oxidation with potassium permanganate (see below) yielded no trace of the characteristic crystalline oxidation products of α-terpinene, whence it appears that the latter terpene had been completely eliminated by the treatment. The chromic acid mixture recovered yielded, on extraction with ether, a small quantity of a crystalline acid melting at 189°, which proved to be one of the forms of αδ-dihydroxy-α-methyl-δ-isopropyladipic acid produced by the oxidation of α-terpinene (see below).

Action of Bromine. Isolation of a New Terpene Tetrabromide.— Bromine, in excess of that required to form a tetrabromide, was added to either the original mixture of hydrocarbons or the α-terpinene-free mixture (see preceding paragraph) dissolved in its own volume of chloroform and cooled to 0°. After standing for one hour, the chloroform and excess of bromine were removed by a current of dry air, leaving a viscous, dark grey oil; this, on standing for six to eight weeks, deposited a solid tetrabromide,

which after solution in ethyl acetate separated in large crystals up
to about 1 gram in weight. The bulk of the brominated product
remained liquid even after six months' exposure to a temperature
of $-15°$ to $-20°$, but on distillation under reduced pressure it
yielded a considerable quantity of p-cymene (b. p. 175—176°), and
the residue, on standing, then deposited a further quantity of the
crystalline tetrabromide. The latter melted and decomposed at
117°, and repeated crystallisation from different solvents failed to
change this melting point. Mixtures of equal parts of the tetra-
bromide with the tetrabromides of (a) d-limonene, m. p. 105°,
(b) dipentene, m. p. 126°, (c) terpinolene, m. p. 112°, melted at
(a) 90—95°, (b) 102—105°, (c) 100—104° respectively, so that the
substance is not identical with any of the well-known terpene
tetrabromides. The tetrabromide is optically inactive (Found:
$Br = 69.88$, 70.08. $C_{10}H_{16}Br_4$ requires $Br = 70.17$ per cent.).
It is apparently the formation of this substance on bromination
that led Nelson (*loc. cit.*) to assume that the hydrocarbon fraction
of chenopodium oil contained l-limonene. The tetrabromide of
the latter, however, melts at 104—105°, is optically active ($[\alpha]_D =$
$-73°$), and when crystallised with an equal quantity of d-limonene
tetrabromide gives dipentene tetrabromide, m. p. 126°. In all
these respects the new substance differs from l-limonene tetra-
bromide, and it is probably the tetrabromide of a new lævorotatory
terpene.

The crystallographic examination of the new tetrabromide has
been kindly undertaken for the authors by Dr. G. F. Herbert Smith
of the Natural History Section of the British Museum, who reports
as follows :

" The crystals are monoclinic. The prominent faces parallel to
which the crystals are elongated belong to the form (110) and the
faces observed at the end belong to the forms (001), (101), and ($\bar{1}$11).
The fundamental data are $a : b : c = 1.413 : 1 : 1.471$; $\beta = 99°$ 51'.
The calculated and observed values of the biangular co-ordinates of
the observed forms are given in the following table.

Form.	Calculated.		Observed.	
	ϕ.	p.	ϕ.	p.
110.................	—	—	0° 0'	35° 42'
$\bar{1}$11.................	48° 35'	42° 12'	48° 44'	41° 51'
101.................	—	—	39° 4'	90° 0'
001.................	—	—	80° 5'	90° 0'

" There is an optic axis very nearly perpendicular to the faces of
the form (110) and the double refraction is high.

" The symmetry of the crystals is different from, and the measure-
ments I have made do not harmonise at all with, those recorded by

Hintze for limonene tetrabromide (*Zeitsch. Kryst. Min.*, 1885, **10**, 252)."

No crystalline derivatives with halogen acids or nitrosyl chloride could be obtained from the mixture of hydrocarbons either before or after the removal of the α-terpinene. Sylvestrene yields a crystalline dihydrochloride.

Oxidation with Potassium Permanganate in Acetone. Isolation of p-*Cymene.*

The results recorded above indicate that the hydrocarbon fraction consists of α-terpinene, cymene, and a lævorotatory terpene, which forms an optically inactive, crystalline tetrabromide. It was hoped to obtain further information regarding this terpene by the oxidation of the whole hydrocarbon fraction with potassium permanganate in the cold, since the products of oxidation of α-terpinene under these conditions are well known and p-cymene is not attacked, so that any products of oxidation found other than those obtainable from α-terpinene might be assumed to come from the lævorotatory terpene. The oxidation was carried out in ice-cold water under the conditions prescribed by Wallach for α-terpinene (*Annalen*, 1908, **362**, 297), but it was subsequently found convenient to replace water by acetone. The hydrocarbon fraction (50 c.c.) was dissolved in acetone (150 c.c.) and a saturated solution of potassium permanganate in acetone added, 50 c.c. at a time, until the reagent was no longer decolorised immediately (*A*). After this stage, the oxidation proceeded very slowly and was completed by adding finely powdered permanganate with constant agitation until the liquid remained coloured for twenty-four hours after the last gram had been added (*B*); usually about 150 grams of permanganate were required in all. If the liquid is worked up at stage (*A*), 60 to 70 per cent. by volume of the oil originally used is recovered, and now has physical constants similar to those of the oil recovered after oxidation with cold chromic acid (p. 1717), with the exception that the highest specific rotation found was $-20°$ in place of $-23°$. It roughly corresponds, therefore, with the oxidation of the α-terpinene. The oil recovered at stage (*B*) was optically inactive, and after several distillations over sodium boiled constantly at $175—176°/763$ mm., and had $n_D^{20°}$ $1·49041$ (Found : $C = 89·2$, $89·3$; $H = 10·4$, $10·51$. p-Cymene, $C_{10}H_{14}$, requires $C = 89·57$; $H = 10·43$ per cent.). It yielded p-cymenesulphonic acid (Found : for the barium salt, $Ba = 24·4$. Calc., $Ba = 24·8$ per cent.), and on oxidation with aqueous potassium permanganate solution at $100°$ yielded p-hydroxy*iso*propylbenzoic acid, m. p. $153—154°$ (Found : $C = 66·45$; $H = 6·8$. Calc.,

$C = 66 \cdot 7$; $H = 6 \cdot 7$ per cent.), from which *iso*propenylbenzoic acid (m. p. 255°) was readily obtained by boiling with hydrochloric acid. The usual methods of identifying *p*-cymene are not very satis-factory. Many terpenes yield *p*-cymenesulphonic acid on treat-ment with sulphuric acid, and the authors have found that com-mercial phellandrene, on oxidation with hot permanganate, yields *p*-hydroxy*iso*propylbenzoic acid; special care was therefore taken in this case to prove that the recovered hydrocarbon was actually *p*-cymene. The amount recovered varied from 45 to 50 per cent. (compare p. 1716).

The products of oxidation were isolated by filtering off the manganese dioxide, distilling off the acetone, and steam-distilling the alkaline residue to recover the *p*-cymene. To the aqueous residue in the flask was added the aqueous extract obtained by suspending the manganese dioxide in water and passing through it a vigorous current of steam for two hours. The combined aqueous liquids were then reduced to low bulk in a vacuum and, when cold, extracted with ether, which removed a small amount of a viscous, neutral, yellow oil having a faint odour of mint. The liquid was then acidified and extracted repeatedly with ether, which removed a complex mixture of acids, mostly resinous, from which on standing there separated crystalline material (*A*) amounting to about 2 per cent. by weight of the oil originally used. When no more crystals would separate, the viscous acid resin was filtered off and steam-distilled. The acid distillate was neutralised with sodium hydroxide, evaporated to dryness, and mixed rapidly and completely with the quantity of sulphuric acid, cooled to $-16°$, required to convert the sodium into sulphate, which separated and was rapidly filtered off, leaving the volatile acids (*B*) as a dark brown liquid. The non-volatile residue in the flask was extracted with ether and yielded a large fraction of resinous acids (*C*).

Crystalline Acids (A).—A rapidly filtered solution in boiling water of the mixture of acids deposited, on standing, colourless, prismatic crystals, of which more was obtained by concentration of the mother-liquor in a vacuum. The crops were mixed and recrystallised from boiling water until of constant melting point, 203—204° (corr., decomp.). The acid was sparingly soluble in cold water or alcohol and less soluble in other solvents, and was optically inactive in aqueous solution (Found: $C = 51 \cdot 21$, $51 \cdot 12$; $H = 7 \cdot 72$, $7 \cdot 82$. $C_{10}H_{18}O_6$ requires $C = 51 \cdot 29$; $H = 7 \cdot 69$ per cent. Required for neutralisation, $8 \cdot 57$ c.c. of N-NaOH per gram. $C_8H_{16}O_2(CO_2H)_2$ requires $8 \cdot 55$ c.c. per gram).

The mother-liquor, on further concentration, deposited a second acid crystallising in rosettes of needles, which was recrystallised

from water until the melting point remained constant at 189° (corr., decomp.). This substance was moderately soluble in water, and optically inactive in 5 per cent. aqueous solution (Found: $C = 51·0$, $51·26$; $H = 7·86$, $7·79$. $C_{10}H_{18}O_6$ requires $C = 51·29$; $H = 7·69$ per cent. Required for neutralisation, 8·56 c.c. of N-NaOH per gram. $C_8H_{16}O_2(CO_2H)_2$ requires 8·55 c.c. per gram).

These two acids appear to be identical with the two $\alpha\delta$-dihydroxy-α-methyl-δ-*iso*propyladipic acids, $C_{10}H_{18}O_6$, obtained by Wallach by the oxidation of terpinen-4-ol from marjoram oil (*Annalen*, 1907, **356**, 212), which he describes as melting at 205—206° and 188—189° respectively. The acids decompose on melting and in the authors' experience the melting points can be varied from 203° to 214° and from 188° to 192° respectively by variation in the rate of heating. Wallach described the acid of higher melting point as the active and the other as the inactive acid, apparently because the latter only was produced by the oxidation of α-terpinene, which is itself optically inactive, whilst the active terpinenol from marjoram oil yielded both. The acid should, however, exist in more than one inactive modification, and both forms obtained by the present authors were inactive. It seemed likely that both these acids came from the α-terpinene, and this was confirmed by oxidising α-terpinene (prepared from terpineol) with permanganate in acetone, when the same two acids were obtained.

After the removal of the acid melting at 189°, concentration of the mother-liquor was continued, by slow evaporation at atmospheric temperature, causing the separation of a third substance, which, after several recrystallisations from water, melted at 179° (Found: $C = 50·55$, $50·84$; $H = 7·6$, $7·69$ per cent. Required for neutralisation, 8·38 c.c. of N-NaOH per gram). Mixed with either of the foregoing acids, this substance showed no depression in melting point, and it is probably merely a mixture of both.

Volatile Acids (B).—The dark brown, volatile acids isolated as already described (p. 1720) consisted mainly of acetic acid, since a series of eight fractions of silver salt prepared from them gave the following results: $Ag = 62·5$, $63·7$, $64·4$, $64·7$, $65·1$, $65·2$, $65·3$, $66·1$. Silver acetate, $CH_3·CO_2Ag$, requires $Ag = 64·68$ per cent. There is, however, present in addition a minute amount of an acid crystallising in long, slender needles, m. p. 117°, of which sufficient has not been obtained for examination; it can be isolated by steam-distilling the crude, volatile acids, stopping the distillation when the distillate begins to show only a weak acid reaction to litmus, and then extracting the residual liquor with ether.

Resinous Acids (C).—These form the bulk of the oxidation products and from them no definite substance has so far been obtained.

The only difference observed in the course of the oxidations with permanganate in (a) water and (b) acetone was that in the former case the volatile acids produced included *iso*butyric acid (Found: in the silver salt, Ag = 55·5, 55·7. Calc., Ag = 55·39 per cent.), which was separated from the acetic acid also formed by fractional crystallisation of the anilides, acetanilide, m. p. 114°, separating first from boiling water and *iso*butyranilide, m. p. 102°, last.

Oxidation with permanganate of the hydrocarbon fraction of chenopodium oil from which α-terpinene had been removed (p. 1717) yielded acetic and *iso*butyric acids and the volatile, crystalline acid melting at 117°. The latter appears, therefore, to be the only oxidation product found which may be characteristic of the lævoro-tatory terpene, and so far it has not been possible to obtain it in quantity sufficient for examination. From this terpinene-free fraction of the hydrocarbon mixture 58 per cent. of cymene was recovered on oxidation.

Oxidation of limonene and phellandrene, under the conditions described above, yielded none of the crystalline products obtained from the chenopodium mixture of hydrocarbons, thus confirming evidence already given of the absence of these terpenes from the mixture.

Ascaridole Fraction.

As already stated, fraction (c) consisted almost wholly of ascaridole and on redistillation had b. p. 108—110°/15 mm., $d^{15°}$ 1·0120, $[\alpha]_D^{15°}$ −0·5°, constants which are in good agreement with those already on record (Found : C = 71·63 ; H = 9·45. Calc., C = 71·43 ; H = 9·53 per cent.). As stated above, ascaridole, when heated above 160°, is converted explosively into an isomeric substance, ascaridole glycol anhydride, the temperature rising to about 300°. Nelson found that the action could be readily con-trolled by dropping ascaridole into cymene heated at 150°. The authors found that dilution of ascaridole with any volatile, indifferent solvent boiling at about 130—150°, for example, xylene, will serve equally well. After the reaction is complete, the solvent is distilled off, leaving a residue of the anhydride which can be purified by distillation. It forms a viscous, yellow oil, b. p. 230—245°/755 mm., 122—125°/20 mm.; d^{15} 1·026; $[\alpha]_D^{15}$ −0·72°.

By treatment with steam, the anhydride is converted into ascaridole glycol, which is not volatile in steam, but can be distilled apparently unchanged under reduced pressure. Obtained in this way, it is a heavy, green, viscous oil, b. p. 135—160°/15 mm. (Found : C = 64·55 ; H = 9·74. Calc., C = 64·46 ; H = 9·74 per cent.). It was previously prepared by Nelson (*loc. cit.*) by

shaking ascaridole with ferrous sulphate solution or by hydrating the anhydride by dilute sulphuric acid. The monobenzoate melts at 136—137°, as recorded by Nelson (Found : $C = 70.68$; $H = 7.92$. Calc., $C = 70.34$; $H = 7.55$ per cent.).

Indian Chenopodium Oil.

In connexion with attempts made in recent years to cultivate chenopodium in India for the production of oil, two samples of the drug have been received from Col. A. T. Gage, Director of the Botanical Survey of India. These were labelled *C. ambrosioides* and *C. anthelminticum* and yielded 0·17 and 0·24 per cent. of oil having $d_{15°}^{15°}$ 0·9399, $[\alpha]_D^{15}$ + 0·07°, and $d_{15°}^{15°}$ 0·9080, $[\alpha]_D^{15}$ —9·6° respectively. The quantities obtained were too small for further investigation.

Summary of Results.

1. Chenopodium oil contains minute quantities of the lower fatty acids, chiefly butyric acid, and less than 0·5 per cent. of methyl salicylate. The remainder of the oil consists of at least 60 per cent. of ascaridole with about 5 per cent. of the corresponding glycol and 30 to 40 per cent. of a mixture of hydrocarbons made up approximately of cymene 15 per cent., α-terpinene 5 per cent., and a new lævorotatory terpene, 10 per cent. No evidence has been obtained of the presence in the oil of sylvestrene, limonene, phellandrene, safrole, or camphor, all of which have been suggested or recorded as constituents.

2. The lævorotatory terpene has not been isolated from the mixture of hydrocarbons, but judging from the physical constants of its mixtures with (a) α-terpinene and cymene, and (b) cymene alone, it must have approximately the following characters : b. p. 177—178°/760 mm., $d^{15°}$ 0·847, $[\alpha]_D^{15}$ —57°, n_D^{20} 1·484. It furnishes a well-crystallised tetrabromide, m. p. 117°, which is optically inactive, and on oxidation with permanganate yields acetic and *iso*butyric acids and possibly a volatile, crystalline acid, m. p. 117°, not yet identified. It is interesting to note that Lewinsohn (*Arch. Pharm.*, 1906, **244**, 424) isolated from myrrh oil a terpene having the following constants ; b. p. 78—80°/20 mm., $d^{20°}$ 0·847, $[\alpha]_D^{20}$ + 80°, yielding a tetrabromide, m. p. 115°.

3. On oxidation with permanganate in acetone, α-terpinene yields two forms of αδ-dihydroxy-α-methyl-δ-*iso*propyladipic acid melting at 203—204° and 189° respectively ; the latter has already been obtained by Wallach by oxidation of this terpene with permanganate in water at 0°, and both acids by the same author from the terpinen-4-ol of marjoram oil by the same means. The acid of higher m. p.

is described by Wallach as active, although no determination of the value is given; both acids obtained by the present authors were optically inactive in aqueous solution.

The authors desire to express their cordial thanks to Dr. Herbert Smith for the crystallographic measurements recorded above and to Mr. F. Walton for assistance in the experimental work.
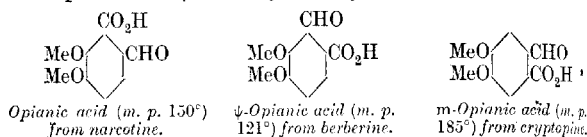
WELLCOME CHEMICAL RESEARCH LABORATORIES.

CXCVII.—m-*Opianic Acid* (4 : 5-*Dimethoxy-o-aldehydobenzoic Acid*).

By ROBERT GEORGE FARGHER and WILLIAM HENRY PERKIN, jun.

THE opianic acids (dimethoxy-o-aldehydobenzoic acids),

Opianic acid (m. p. 150°) from narcotine.   ψ-Opianic acid (m. p. 121°) from berberine.   m-Opianic acid (m. p. 185°) from cryptopine.

have so far only been obtained from alkaloids either by direct oxidation or by the oxidation of their degradation products.

In view of the importance of these acids, it is curious that there should be no record of any attempt having been made to prepare them synthetically. It seemed therefore interesting to devise methods for the synthesis of these acids and the present communication contains an account of the steps which have led to the synthesis of m-opianic acid.* It is hoped that it may, in the near future, be found possible to synthesise opianic acid and ψ-opianic acid as well and thus to complete the series.

The starting point in the synthesis of m-opianic acid is creosol (I), which is first methylated by means of methyl sulphate; the resulting homoveratrole (II) is then converted by the action of acetyl chloride in the presence of aluminium chloride into 4 : 5-dimethoxy-o-tolyl methyl ketone (III)

(I.)   (II.)   (III.)
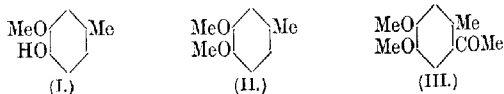
* The name m-opianic acid was given to this acid because it is the opianic acid corresponding with m-hemipinic acid.

(compare Harding and Weizmann, T., 1910, **97**, 1126). When this ketone is oxidised by permanganate, it yields 4 : 5-dimethoxy-*o*-tolylglyoxylic acid (IV), 4 : 5-dimethoxyphthalonic acid (V), and *m*-hemipinic acid (VI).

MeO⟨ ⟩Me   MeO⟨ ⟩CO_2H MeO⟨ ⟩CO_2H
MeO⟨ ⟩$CO \cdot CO_2H$ MeO⟨ ⟩$CO \cdot CO_2H$ MeO⟨ ⟩CO_2H

  (IV.)   (V.)   (VI.)
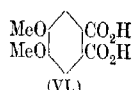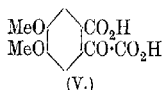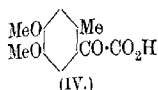
4 : 5-Dimethoxyphthalonic acid (V) was first obtained by Perkin (T., 1902, **81**, 1022) during the investigation of the oxidation of trimethylbrazilin by means of permanganate, and was stated to melt at 150°. Subsequently Harding and Weizmann (*loc. cit.*, p. 1129) prepared the same acid * from 4 : 5-dimethoxy-*o*-tolyl methyl ketone by oxidation with permanganate, and these investigators found that a specimen of the acid dried in the steam-oven melted at 148°. These observations are incorrect, and the reason for the inaccuracy is to be found in the facts (i) that the acid, like phthalonic acid itself, has no definite melting point, and (ii) that the indefinite melting point is lowered by traces of moisture and slight impurity to an unusual degree.

We have, on several occasions, repeated the preparation of 4 : 5-dimethoxyphthalonic acid under the conditions recommended by Harding and Weizmann, and have always obtained an acid which crystallised well from water and melted roughly at 145—150°. It was then found that the acid prepared in this way invariably contains traces of oxalic acid, which apparently cannot be removed by recrystallisation, and the purification by means of the calcium salt, recommended in this case and in the case of the acid from trimethylbrazilin, is of no avail, since both acids yield calcium salts which are insoluble in water. Subsequently the observation was made that the insoluble *neutral* calcium salt of 4 : 5-dimethoxyphthalonic acid, $\dfrac{(MeO)_2C_6H_2 \cdot CO \cdot O}{CO-CO-O}{>}Ca$, is converted by the calculated amount of dilute hydrochloric acid into a beautifully crystalline, soluble *acid* calcium salt, $(C_{11}H_9O_7)_2Ca$, whereas calcium oxalate remains unchanged, and this observation has made it possible to prepare the phthalonic acid readily in a state of purity.

4 : 5-Dimethoxyphthalonic acid crystallises from water in prisms usually of the composition $C_{11}H_{10}O_7, 2H_2O$, and does not melt completely until 188° (compare p. 1736). When it is heated in the steam-oven, it loses one molecule of water, but the other is not lost at 120°, and does not seem to be removable by heat without

* Called by them 6-carboxy-3 : 4-dimethoxyphenylglyoxylic acid.

decomposition of the acid. It is therefore probable that the formula of the hydrated acid, crystallised from water and dried at 100°, is $(MeO)_2C_6H_2(CO_2H)\cdot C(OH)_2\cdot CO_2H$. On the other hand the acid is somewhat soluble in dry ether and, after digesting with anhydrous sodium sulphate and concentrating, it separates in colourless prisms which are anhydrous and have the formula $C_{11}H_{10}O_7$.

This acid now crystallises from water in *anhydrous* prisms, and it seems possible that the hydrated acid is derived from V, whereas the anhydrous acid has the constitution XVII. This interesting point is being investigated.

When 4 : 5-dimethoxyphthalonic acid is heated at 200—210°, it is completely decomposed, with the formation mainly of *m*-hemipinic acid, but small quantities of the anhydride of *m*-opianic acid (p. 1742) are produced, as well as traces of a substance melting above 260°, which appears to be *tetramethoxydiphthalyl,*

$$(MeO)_2C_6H_2-\underset{\underset{\displaystyle CO}{|}}{C}=\underset{\underset{\displaystyle O}{|}}{C}-C_6H_2(OMe)_2 \ ,$$
$$CO——O \quad O—CO$$
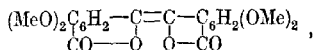
and to be identical with the substance, $C_{20}H_{16}O_8$, which had previously been obtained (Perkin, T., 1902, **81**, 1025) from the same acid by heating with water in a sealed tube at 200°. In this behaviour, dimethoxyphthalonic acid resembles phthalonic acid itself, which, on heating, is decomposed into phthalic anhydride, phthalaldehydic acid, and diphthalyl (Graebe and Trümpy, *Ber.,* 1898, **31**, 371). When 4 : 5-dimethoxyphthalonic acid is heated with concentrated sulphuric acid on the steam-bath, it is decomposed, apparently quantitatively, into carbon monoxide and *m*-hemipinic acid.

The conversion of 4 : 5-dimethoxyphthalonic acid into m-*opianic acid* has been carried out in two different ways :

(i) *By Heating with Sodium Hydrogen Sulphite.*—In this case the sodium hydrogen sulphite derivative of the phthalonic acid, which is first produced, is decomposed by heating on the steam-bath into carbon dioxide and the corresponding derivative of *m*-opianic acid. When the latter is treated with hydrochloric acid and the product extracted with ether, *m*-opianic acid crystallises from the ether in a state of purity.

(ii) *With the Aid of Aniline or* p-*Toluidine* (p. 1740).—Aniline reacts very readily with a hot aqueous solution of 4 : 5-dimethoxyphthalonic acid with separation of a crystalline substance (m. p. 179—180°) which is the *aniline* salt of *anilino-*4 : 5-*dimethoxyphthalonic acid* and probably has the formula

$$(MeO)_2C_6H_2(CO_2H)\cdot C(:N\cdot C_6H_5)\cdot CO_2H,C_6H_5\cdot NH_2.$$
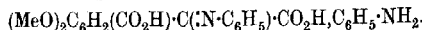
When this is boiled with xylene, it loses carbon dioxide and the substance which crystallises from the xylene and melts at 213—214°, is *anilino-*m-*opianic acid*, $(MeO)_2C_6H_2{<}^{CH(NH \cdot C_6H_5)}_{CO-\underline{\quad\quad}}{>}O$ (compare p. 1738). Warm dilute hydrochloric acid readily hydrolyses this anilino-derivative with formation of aniline hydrochloride and *m*-opianic acid, and as the decomposition is quantitative and the acid crystallises direct in an almost pure state from the hydrochloric acid, this is much the most convenient method for the preparation of *m*-opianic acid. In the case of *p*-toluidine, the course of the different reactions is similar. The substance first produced is the *p-toluidine* salt of *p-toluidino*-4 : 5-*dimethoxyphthalonic acid*, and this, on boiling with xylene, yields *p-toluidino*-m-*opianic acid* (m. p. 223°), from which *m*-opianic acid is obtained by hydrolysis with dilute hydrochloric acid. There is not much to choose between the aniline and *p*-toluidine processes, but the latter was preferred and employed for the preparation of most of the *m*-opianic acid required for this investigation.

m-Opianic acid melts at 186—187° or considerably higher than either opianic acid (m. p. 150°) or ψ-opianic acid (m. p. 121°); like opianic acid, it is very sparingly soluble in cold water and indeed in nearly all its properties and reactions it resembles opianic acid very closely. Some of the more characteristic derivatives of *m*-opianic acid were prepared from the specimen of this acid which was originally obtained by the oxidation of cryptopidene (T., 1916, **109**, 929), and these are the following :

The oxime (m. p. 140°) and the oxime anhydride (m. p. 132—133°), both of which on heating pass into *m*-hemipinimide :

$$(MeO)_2C_6H_2{<}^{CH\vdots NOH}_{CO_2H} \rightarrow (MeO)_2C_6H_2{<}^{CH\vdots N}_{CO-O} \rightarrow$$
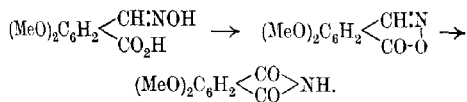
$$(MeO)_2C_6H_2{<}^{CO}_{CO}{>}NH.$$

The semicarbazone, $(MeO)_2C_6H_2(CO_2H) \cdot CH \vdots N \cdot NH \cdot CO \cdot NH_2$, melts at 227°.

m-Opianic acid was also reduced to *m*-meconine and yielded, on acetylation, acetyl-*m*-opianic acid (m. p. 159°).
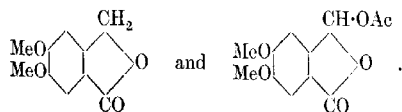
The formation of the latter substance suggests that *m*-opianic acid is capable of reacting in two different modifications, namely,

as the *normal* acid (VII) and as the *pseudo*-acid or derivative of hydroxyphthalide (VIII),

MeO⟨ ⟩CHO
MeO⟨ ⟩CO$_2$H

(VII.)

CH·OH

MeO⟨ ⟩O
MeO⟨ ⟩
        CO

(VIII.)
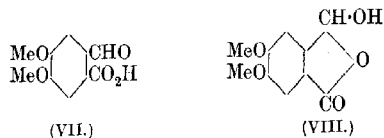
and much new material has now been accumulated which shows clearly how very closely opianic acid and *m*-opianic acid resemble each other in this respect. One of the most characteristic properties of opianic acid is that of yielding two series of esters, namely, the *normal* carboxylic esters and the *pseudo*-esters derived from the hydroxyphthalide formula and containing the grouping >CH(OMe).

An exactly similar property is exhibited by *m*-opianic acid. When the silver salt of this acid is digested with methyl iodide, the methyl ester formed is the *normal* ester (IX; m. p. 95°), but the *pseudo*-methyl ester (X; m. p. 143°) is produced when *m*-opianic acid is boiled with methyl alcohol.

MeO⟨ ⟩CHO
MeO⟨ ⟩CO$_2$Me

(IX.)

CH·OMe

MeO⟨ ⟩O
MeO⟨ ⟩
        CO

(X.)
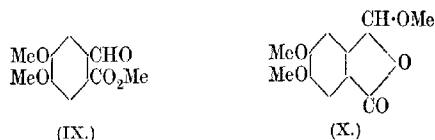
In cases other than that of the isomeric esters, opianic acid yields derivatives both of the *normal* and *pseudo*-modification.

Towards semicarbazide, this acid behaves as the aldehyde, but Liebermann (*Ber.*, 1896, 29, 174) has shown that the action of aniline and other amino-compounds on the acid results in the formation of crystalline substances which are always derivatives of the *pseudo*-modification. Thus the anilino-derivative (m. p. 187°) is insoluble in cold dilute sodium carbonate and cannot therefore be the normal derivative (XI), but must have the constitution represented by (XII).

CO$_2$H

MeO⟨ ⟩CH:N·C$_6$H$_5$
MeO⟨ ⟩

(XI.)

CO
    ⟩O
MeO⟨ ⟩ CH·NH·C$_6$H$_5$
MeO⟨ ⟩

(XII.)
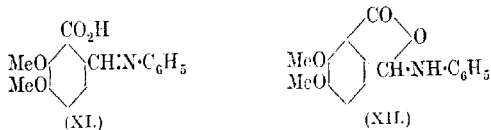
A careful investigation has shown that *m*-opianic acid behaves in these respects exactly like opianic acid. The semicarbazone of *m*-opianic acid is evidently derived from the normal acid, because

it is immediately soluble in cold sodium carbonate solution.   Aniline and p-toluidine react very readily with aqueous or alcoholic solutions of m-opianic acid, yielding immediate, crystalline precipitates of the anilino- and p-toluidino-derivatives, which melt at 213° and 222° respectively and are insoluble in cold dilute sodium carbonate solution.

The constitutions of these substances must therefore be represented by the formulæ :

$$CH \cdot NH \cdot C_6H_5$$

MeO / MeO — ⬡ — O — CO

(XIII.)   and

$$CH \cdot NH \cdot C_6H_4Me$$

MeO / MeO — ⬡ — O — CO

(XIV.)
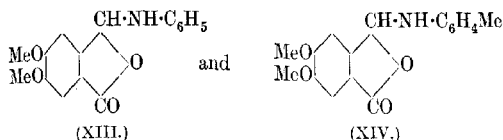
It is remarkable that the substance (m. p. 213°) produced by the action of aniline on m-opianic acid should prove to be identical with that which results when the anilino-derivative of 4 : 5-dimethoxyphthalonic acid is heated with xylene (p. 1727).   It is clear that the change

MeO / MeO — ⬡ — $C(:N \cdot C_6H_5) \cdot CO_2H$ / CO_2H →   MeO / MeO — ⬡ — $CH:N \cdot C_6H_5$ / CO_2H

(XV.)
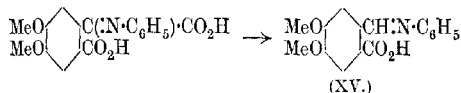
does not accurately represent the decomposition, and it must therefore be assumed either that formula XV undergoes molecular change into XIII or that the anilino-derivative of the phthalonic acid has the constitution XVI.

$$C(NH \cdot C_6H_5) \cdot CO_2H$$

MeO / MeO — ⬡ — O — CO

(XVI.)

$$C(OH) \cdot CO_2H$$

MeO / MeO — ⬡ — O — CO
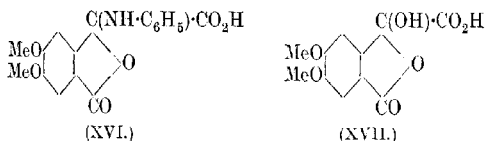
(XVII.)

It is also, of course, possible that the phthalonic acid itself is capable of reacting in the pseudo-form XVII, in which case the anilino-derivative would be XVI and its conversion into XIII as the result of loss of carbon dioxide would follow as a matter of course.

In one respect, opianic acid and m-opianic acid exhibit a striking and unexpected difference, and that is in their behaviour with phenylhydrazine.   When a warm aqueous solution of opianic acid is mixed with phenylhydrazine, it yields an oily, yellow *hydrazone*

which very rapidly becomes crystalline owing to the conversion into *phenylopiazone* (m. p. 175°; p. 1744):

$$\underset{MeO}{\overset{CO_2H}{\underset{MeO}{}}}\!\!\left<\text{CH:N·NH·C}_6\text{H}_5 \right. \longrightarrow \underset{MeO}{\overset{CO}{\underset{MeO}{}}}\!\!\left<\text{CH:N·N·C}_6\text{H}_5 \right. .$$

In the case of *m*-opianic acid, the yellow, crystalline *hydrazone* (XVIII) is remarkably stable, and may indeed be crystallised from methyl alcohol. At 185—190°, however, it becomes colourless owing to the formation of *phenyl*-m-*opiazone* (XIX) (m. p. 228°; p. 1743):

$$\underset{MeO}{\overset{MeO}{}}\!\!\left<\begin{array}{l}\text{CH:N·NH·C}_6\text{H}_5\\ \text{CO·OH}\end{array}\right. \longrightarrow \underset{MeO}{\overset{MeO}{}}\!\!\left<\begin{array}{l}\text{CH:N·N·C}_6\text{H}_5\\ \text{—CO}\end{array}\right. .$$

$$\text{(XVIII.)} \qquad\qquad\qquad \text{(XIX.)}$$

Both opianic and *m*-opianic acids react with *as*-phenylmethyl-hydrazine to produce stable derivatives of the formula
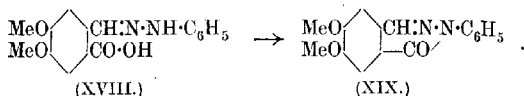
$$(\text{MeO})_2\text{C}_6\text{H}_2(\text{CO}_2\text{H})\cdot\text{CH:N·NMe·C}_6\text{H}_5$$

(m. p. 167° and 237° respectively), which, owing to the presence of the *N*-methyl group, are incapable of yielding derivatives of the type phenylopiazone.

EXPERIMENTAL.

Homoveratrole (Formula II).

Homoveratrole was first obtained by Tiemann and Mendelsohn (*Ber.*, 1875, **8**, 1137) by the action of methyl iodide on the potassium derivative of creosol [CH$_3$·C$_6$H$_3$(OMe)·OH $=1:3:4$], and later (T., 1906, **89**, 1649) Perkin and Weizmann simplified the process by substituting methyl sulphate for the methyl iodide.* In preparing the large quantities of material required for the present investigation, the following method was found to work well. The solution of creosol (50 grams) in methyl alcohol (150 c.c.) was gradually mixed with methyl sulphate (60 c.c.) and methyl-alcoholic potassium hydroxide (180 c.c. of 25 per cent.), and so soon as the reaction had subsided the whole was heated on the steam-bath for a few minutes, cooled, diluted with water, rendered strongly alkaline by the addition of sodium hydroxide, and extracted with ether. The extract was dried over potassium carbonate, the ether

* There is an error in the quantities given for the preparation of veratrole from catechol; the amount of methyl sulphate should be 275 grams, and not 75 grams.

removed, and the residue fractionated, when about 45 grams of homoveratrole distilled at 128—130°/25 mm. and some unchanged creosol was recovered from the alkaline liquors.

It was noticed that homoveratrole, after standing in the ice-chest for some days, had solidified to a mass of striated prisms; after purification by partial melting and decantation of the melted portion, the crystals melted at about 22°.

4 : 5-*Dimethoxy-o-tolyl Methyl Ketone* (Formula III).

Harding and Weizmann (T., 1910, **97**, 1127) obtained this substance by acting on homoveratrole and acetyl chloride, dissolved in carbon disulphide, with aluminium chloride, but we have obtained a larger yield and a purer product by allowing the aluminium chloride to react first with the acetyl chloride and afterwards adding the homoveratrole.

Freshly-prepared and finely-powdered aluminium chloride (100 grams) is gradually added to the well-cooled solution of acetyl chloride (30 grams) in carbon disulphide (200 c.c.) and, after standing for half an hour, homoveratrole (50 grams) is slowly run in, with constant stirring and cooling in ice-water. After remaining over-night, the mixture is heated on the steam-bath until hydrogen chloride ceases to be evolved, the carbon disulphide removed by distillation, and the residue decomposed by much powdered ice. The product is extracted with ether, the ethereal solution well washed with dilute hydrochloric acid and repeatedly shaken with 5 per cent. sodium hydroxide so long as the extract (A) is brown; it is then dried over calcium chloride, concentrated to a small bulk, and left in the ice-chest, when a crust of prisms quickly separates. The mother-liquor is decanted and the crystals are washed with a little ether with suction; the substance then melts at 76—77°, and consists of pure 4 : 5-dimethoxy-o-tolyl methyl ketone.

The ethereal filtrate is evaporated and the residue fractionated under reduced pressure, when, after traces of homoveratrole have passed over, the whole distils at 175°/15 mm. and crystallises on cooling.

The ketone is rather sparingly soluble in cold methyl alcohol, but dissolves very readily on warming, and separates, when slowly cooled, in large, almost colourless, glistening prisms which do not lend themselves to accurate crystallographical measurement. The yield is about equal to the amount of homoveratrole employed in the synthesis.

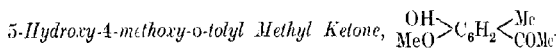The *oxime* was obtained by boiling the ketone (1·4 grams) with

hydroxylamine hydrochloride (1 gram) in alcoholic solution in the presence of excess of sodium acetate. Water was added, when, on standing, the oxime separated in colourless prisms which, after recrystallisation from water, melted at 138° (Found : $N = 6.8$. $C_{11}H_{15}O_3N$ requires $N = 6.7$ per cent.).

The semicarbazone was prepared by boiling the ketone (1 gram) with semicarbazide hydrochloride (1·2 grams) and sodium acetate (3 grams) in aqueous alcohol for half an hour. On cooling, the semicarbazone separated, and was recrystallised from alcohol, when it melted at 208°. Harding and Weizmann (*loc. cit.*, p. 1128) state that it decomposes at 186° (Found : $N = 16.8$. Calc., $N = 16.7$ per cent.).

The phenylhydrazone separated gradually in crystals when the ketone was heated on the steam-bath with phenylhydrazine in dilute acetic acid solution. It was collected with the aid of the pump and washed with methyl alcohol, in which it was sparingly soluble. The colourless, crystalline residue melted without decomposition at 182°, whereas Harding and Weizmann (*loc. cit.*, p. 1128) state that this phenylhydrazone melts at 168—170° with decomposition (Found : $N = 10.5$. Calc., $N = 10.4$ per cent.).

The *benzylidene* derivative, $(MeO)_2C_6H_2Me \cdot CO \cdot CH\!:\!CH \cdot C_6H_5$, separated as a mass of crystals when the solution of the ketone and benzaldehyde in a small quantity of methyl alcohol was mixed with a few drops of 50 per cent. potassium hydroxide and allowed to stand. After crystallisation from alcohol, from which it separated in needles, it melted at 110° (Found : $C = 76.8$; $H = 6.5$. $C_{18}H_{18}O_3$ requires $C = 76.6$; $H = 6.4$ per cent.).

The *piperonylidene* derivative, prepared in a similar manner, crystallises from alcohol and melts at 109°.

5-Hydroxy-4-methoxy-o-tolyl Methyl Ketone, $\begin{smallmatrix}OH\\MeO\end{smallmatrix}\!>\!C_6H_2\!<\!\begin{smallmatrix}Me\\COMe\end{smallmatrix}$

This substance, produced during the interaction of acetyl chloride with homoveratrole in the presence of aluminium chloride, is extracted from the main product of the reaction with sodium hydroxide (A, p. 1731).

The deep brown, alkaline extract is acidified, when an oil separates which soon solidifies to a brown mass ; this is collected, washed, and extracted several times with boiling water. The aqueous extract, after decolorising with animal charcoal, deposits a mass of glistening crystals, and a further considerable crop is obtained by concentrating the filtrate on the steam-bath under reduced pressure. Finally, the substance is crystallised either from much light petroleum or from a mixture of benzene and light petroleum,

n which it is more soluble, and from which it separates in colour-ess, glistening, fern-like masses (Found: $C = 66.3$; $H = 6.8$. $C_{10}H_{12}O_3$ requires $C = 66.6$; $H = 6.7$ per cent.). A Zeisel deter-mination gave $OMe = 16.7$, whereas $C_{10}H_{12}O_3$ containing 1OMe requires $OMe = 17.2$ per cent.

5-Hydroxy-4-methoxy-o-tolyl methyl ketone melts at 123° and is sparingly soluble in water or light petroleum, but dissolves readily n methyl alcohol or benzene. The solution in methyl alcohol gives with ferric chloride a rather faint yellowish-green coloration.

The *phenylhydrazone* was prepared by adding the hydroxy-ketone (1 gram) to a solution of phenylhydrazine (3 grams) in 50 per cent. acetic acid and heating on the steam-bath for a few minutes. The yellow solution clouded on cooling and gradually deposited the hydrazone as a crystalline mass, which was collected and recrystallised from methyl alcohol, in which it was sparingly soluble in the cold and from which it separated in glistening prisms melting at 164—165° (Found: $N = 10.4$. $C_{16}H_{18}O_2N_2$ requires $N = 10.4$ per cent.).

The Semicarbazone.—The hydroxy-ketone dissolves in a hot strong solution of semicarbazide acetate and, on standing, groups of prisms slowly separate. This semicarbazone softens at 220° and decomposes at about 228—230°; it is sparingly soluble even in boiling water, but dissolves readily in dilute sodium hydroxide solution (Found: $N = 17.7$. $C_{11}H_{15}O_3N_3$ requires $N = 17.7$ per cent.).

The *piperonylidene* derivative,

$$MeO \cdot C_6H_2Me(OH) \cdot CO \cdot CH:CH \cdot C_6H_3:O_2:CH_2,$$
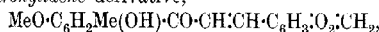
i readily prepared by boiling the hydroxy-ketone with a methyl-alcoholic solution of piperonal and rather more than one molecular proportion of potassium hydroxide for twenty minutes. After most of the methyl alcohol has been distilled off under reduced pressure, dilute hydrochloric acid is added, and the solid mass crystallised from alcohol, from which it separates in yellow needles melting at 158° (Found: $C = 69.0$; $H = 5.2$. $C_{18}H_{16}O_5$ requires $= 69.2$; $H = 5.2$ per cent.).

The Acetyl Derivative.—In preparing this derivative, the hydr-oxy-ketone was boiled with excess of acetyl chloride for half an hour and the excess distilled from the clear solution, when a syrup remained which soon crystallised. The whole was stirred with a little methyl alcohol, in which the acetyl derivative was sparingly soluble, filtered with the aid of the pump, and recrystallised from methyl alcohol, from which the acetyl derivative separated in prismatic needles melting at 108° (Found: $C = 64.8$; $H = 6.5$. $C_{12}H_{14}O_4$ requires $C = 64.8$; $H = 6.3$ per cent.).

Methylation of the Hydroxy-ketone.—The ketone (1 gram), suspended in a little methyl alcohol, was gradually mixed with methyl sulphate (1·5 c.c.) and methyl-alcoholic potassium hydroxide (5 c.c. of 25 per cent.), and, after remaining for an hour, the whole was heated on the steam-bath for ten minutes.   On the addition of water, a mass of needles gradually separated, and this was collected and recrystallised from a little methyl alcohol, from which the substance separated in small prisms melting at 76°. That this substance is 4 : 5-dimethoxy-*o*-tolyl methyl ketone (m. p. 76—77°; p. 1731) was shown by careful comparison and by the method of mixed melting points.   The conversion under the conditions described above is almost quantitative.

Oxidation of 4 : 5-Dimethoxy-o-tolyl Methyl Ketone.

The main object of the study of this oxidation was to discover the conditions for the preparation of 4 : 5-dimethoxy-*o*-phthalonic acid in a state of purity.   It is explained in the introduction (p. 1725) that the oxidation of this ketone by means of permanganate leads to the formation, not only of the acid just mentioned, but also of 4 : 5-dimethoxy-*o*-tolylglyoxylic acid, *m*-hemipinic acid, and oxalic acid, and the complete separation of the phthalonic acid from oxalic acid proved to be particularly difficult.   As the result of a series of comparative experiments, the following process has now been devised, which yields the phthalonic acid without difficulty in a state of purity.   A flask containing water (200 c.c.), potassium carbonate (10 grams), and the ketone (20 grams), and fitted with a vigorously acting stirrer, is heated on the steam-bath until the ketone has melted, the source of heat is then removed, and a solution of potassium permanganate (75 grams) in boiling water (800 c.c.) run in rather rapidly.   The oxidation appears to take place in distinct stages, the first probably being the oxidation of the acetyl group and the second that of the methyl group.   At first the permanganate is very rapidly reduced, sufficient heat being developed to cause the li:.uid to boil vigorously; at the second stage, the action is much less rapid and the flask may be replaced on the steam-bath to complete the action.

The whole is filtered with the aid of the pump, and the faintly coloured filtrate and washings of the manganese precipitate are mixed with hydrochloric acid until the yellow colour produced just persists; the liquid is now acid to litmus, but does not react with Congo-paper.   After concentrating considerably on the steam-bath, the hot liquid, which is now acid to Congo-paper, is made strongly alkaline with ammonia, mixed with calcium chloride

(40 grams) dissolved in a little water, and, while still hot, the granular precipitate is collected with the aid of the pump and washed with hot water (filtrate B). The residue, a mixture of the calcium salt of the phthalonic acid and calcium oxalate, is stirred with hot water and dilute hydrochloric acid until the liquid is just (but distinctly) acid to Congo-paper. In this way the insoluble neutral calcium salt of the phthalonic acid is converted into the soluble acid salt, whereas the calcium oxalate remains unchanged.

After filtering from the calcium oxalate, the filtrate is evaporated to a small bulk, when, on standing, the *acid calcium* salt separates splendidly as a hard crust of prisms; it is collected (C) and allowed to dry in the air. Analysis showed that this salt, dried at 100°, is anhydrous [Found : Ca = 7·5. $(C_{11}H_{10}O_6)_2$Ca requires Ca = 7·3 per cent.].

This salt is rather readily soluble in boiling water, but sparingly so in the cold, and when the hot solution is decomposed with a considerable excess of hydrochloric acid (the phthalonic acid is much less soluble in hydrochloric acid than in water), the solution gradually deposits the pure acid in crusts of pale amber prisms. A large crop of crystals of the same acid is also obtained when the filtrate from the calcium salt (C) is mixed with excess of hydrochloric acid and allowed to stand. The filtrate (B) from the neutral calcium salts is concentrated considerably, when, on standing, a crust of calcium salt separates. This salt is very sparingly soluble in boiling water, but readily so in hot dilute hydrochloric acid, and, on cooling, an acid separates in pale ochre *needles* which melt at 202—204° with vigorous effervescence, and this was found to be *m*-hemipinic acid.* On mixing the filtrate from the calcium salt of this acid with a large excess of hydrochloric acid, a turbidity was produced and soon a large quantity of a crystalline acid separated which, after recrystallisation from hot water, melted at 155° and proved to be 4 : 5-dimethoxy-*o*-tolylglyoxylic acid, $(MeO)_2C_6H_2Me\cdot CO\cdot CO_2H$ (Harding and Weizmann, T., 1910, **97**, 1128).

After working up the mother-liquors, the yields of the various

* (Found : C = 53·2; H = 4·5. $C_{10}H_{10}O_6$ requires C = 53·1; H = 4·4 per cent.). At certain concentrations, *m*-hemipinic acid separates in groups of *prisms* without water of crystallisation, and, if rapidly heated, these melt at 189—190° with vigorous decomposition (compare Dobbie and Lauder, T., 1899, **75**, 677). The behaviour of the acid with ammoniacal calcium chloride is characteristic. If the strongly alkaline solution of the ammonium salt is mixed with calcium chloride, there is no immediate precipitate, but the solution will soon gelatinise, and, on boiling, the sparingly soluble calcium salt separates in a crystalline form.

substances obtained from the product of the oxidation of 60 grams
of 4 : 5-dimethoxy-o-tolyl methyl ketone were as follows :

4 : 5-Dimethoxyphthalonic acid	40 grams
4 : 5-Dimethoxy-o-tolylglyoxylic acid	16 ,,
m-Hemipinic acid	1·5 ,,
Calcium oxalate	4·5 ,,

If the oxidation had proceeded completely from the ketone to the
phthalonic acid, the yield of the latter should have been about
80 grams.

4 : 5-*Dimethoxyphthalonic Acid* (Formula V).

This acid is almost miscible with boiling water, and the pale
amber prisms which separate on cooling contain two molecules of
water, since, on analysis, the air-dry substance gave $C = 45·8$,
$45·7$; $H = 5·0$, $5·1$, whereas $C_{11}H_{10}O_7,2H_2O$ requires $C = 45·6$;
$H = 4·9$ per cent. When the crystals are heated in the steam-oven,
they readily lose 1 mol. of water (Found : loss $= 6·7$. $C_{11}H_{10}O_7,2H_2O$,
losing $1H_2O$, requires loss $= 6·3$ per cent.) and the acid then gave
$C = 48·6$; $H = 4·6$, whereas $C_{11}H_{10}O_7,H_2O$ requires $C = 48·5$;
$H = 4·4$ per cent.

There is no further loss on heating at 120°, indicating that the
remaining molecule of water is constitutional.* The acid has no
definite melting point. If the crystals containing $2H_2O$ are rapidly
heated in a capillary tube, they soften at 100°, become yellow, and
are partly melted at 150°, but fusion is not complete until 187°,
when decomposition takes place with evolution of gas (see below)
and formation of a yellow syrup. After the hydrated acid has
been thoroughly dried in the steam-oven, there is no softening
below 150°, but above this temperature the acid becomes yellow,
gradually softens, and melts at 188° with decomposition.

It was subsequently found possible to prepare the unhydrated
phthalonic acid by digesting the hydrated acid with much ether,
in which it is very sparingly soluble, and anhydrous sodium sulphate
on the steam-bath for two hours. After remaining for two days
with frequent shaking, the ethereal solution was concentrated
considerably, when, on standing, a crust of colourless prisms
separated (Found : $C = 52·0$; $H = 4·0$. $C_{11}H_{10}O_7$ requires $C = 52·0$; $H = 3·9$ per cent.).

This specimen of anhydrous 4 : 5-dimethoxyphthalonic acid
softened and became gradually yellow above 170° and melted at

* The statement (T., 1902, **81**, 1023) that this acid loses two molecules
of water at 100° is incorrect.

about 187° with decomposition. It is curious that the anhydrous acid is sparingly soluble in cold water and dissolves only gradually on warming, whereas the hydrated acid is very readily soluble in water (see p. 1726).

Decomposition by Heat.—If the crystals, $C_{11}H_{10}O_7,2H_2O$, are heated in a test-tube at 200—210° in a sulphuric acid bath, the melted mass becomes yellow, gives off water and a little carbon dioxide, but the gas does not burn, and no direct experiment has been made to demonstrate the presence of carbon monoxide. A small sublimate, probably consisting of tetramethoxydiphthalyl (p. 1726), is deposited in yellow needles on the portion of the tube actually in the hot sulphuric acid.

The yellowish-brown melt, which solidified completely, was boiled with a considerable volume of water, when a cloudy liquid was produced which, on cooling, deposited a small quantity of a red-ochreous mass. This was collected (A) and recrystallised from glacial acetic acid, in which the substance was very sparingly soluble and from which it separated in pale yellow crystals melting above 250°. This substance is probably identical with the substance, $C_{20}H_{16}O_8$, previously obtained (Perkin, T., 1902, **81**, 1025) by heating 4 : 5-dimethoxyphthalonic acid with water in a sealed tube at 200°, and there can be little doubt that it is tetramethoxydiphthalyl (compare p. 1726). It dissolves in concentrated sulphuric acid, yielding an intense purple solution, and the addition of a drop of nitric acid changes the colour to deep bluish-violet. The aqueous filtrate (A) from this substance was concentrated considerably, when it deposited a very small quantity of the anhydride of *m*-opianic acid in needles melting at 230°. On remaining exposed to the air, the filtered solution gradually deposited pale amber prisms, which melted at 188—190° and consisted of *m*-hemipinic acid, and this acid is the main product of the decomposition. It was curious that the mother-liquor from this acid, on long standing, gradually deposited a small quantity of the much less soluble *m*-opianic acid.

Action of Sulphuric Acid.—4 : 5-Dimethoxyphthalonic acid is coloured orange-red by sulphuric acid, and, on warming in the steam-bath, the solution becomes deep reddish-brown and effervesces owing to the escape of carbon monoxide. On diluting with water, the colour is discharged and the liquid sets to a mass of crystals of *m*-hemipinic acid which, in this case, separated from water in needles melting at 200—202°.

Action of Aniline on 4 : 5-Dimethoxyphthalonic Acid. Formation of the Aniline Salt of Anilino-4 : 5-dimethoxyphthalonic Acid,
$(MeO)_2C_6H_2(CO_2H)\cdot C(:N\cdot C_6H_5)\cdot CO_2H, C_6H_5\cdot NH_2.$

The hot aqueous solution of 4 : 5-dimethoxyphthalonic acid (2·5 grams) reacts readily with aniline (3 c.c.), and if the cloudy liquid is kept at 80—90°, a mass of crystals of the above aniline salt will soon separate.

This is collected with the aid of the pump and washed well with water and then with benzene, which removes all the coloured impurity and leaves the pure aniline salt as a colourless, crystalline mass melting with vigorous decomposition at 179—180°. The yield is about 1·8 grams (Found : C = 65·4; H = 5·4; N = 6·4. $C_{23}H_{22}O_6N_2$ requires C = 65·4; H = 5·2; N = 6·6 per cent.). This substance is rather sparingly soluble in methyl alcohol in the cold, but dissolves readily on boiling and separates in glistening laminæ. It is almost insoluble in benzene or light petroleum, and rather sparingly so in cold acetone, from which, however, it crystallises well. It dissolves in hot glacial acetic acid, but nothing separates on cooling or diluting with water. Dilute hydrochloric acid colours it yellow, and on warming a clear, colourless solution results, from which nothing separates on cooling.

The crystals of the aniline salt dissolve readily in concentrated sulphuric acid to a deep orange-red solution.

The aniline salt is decomposed by cold sodium hydroxide solution with the separation of aniline, and it is interesting, as showing the great tendency to form this salt, that if the liquid is now rendered faintly acid with hydrochloric acid, the aniline salt again separates, melting at 178° (Found : N = 6·2 per cent.). If, however, the aniline is removed from the alkaline solution by extraction with ether, hydrochloric acid precipitates a viscous acid which gradually sets to a resin, and this substance is presumably anilino-4:5-dimethoxyphthalonic acid, but it was not further investigated.

The aniline salt decomposes on heating at 180—190° with elimination of carbon dioxide, and the residual resin crystallises from methyl alcohol, melts at about 190° to a cloudy syrup, and consists of slightly impure anilino-*m*-opianic acid (see below).

This substance was subsequently prepared in considerable quantity in the following way. The aniline salt (2 grams) is almost insoluble in pure xylene (20 c.c.), but, on boiling in a reflux apparatus for half an hour, carbon dioxide is eliminated and a clear yellow solution obtained. On cooling, a mass of crystals separates, and these are collected and boiled with much methyl alcohol in order

to separate the anilino-derivative from a very sparingly soluble substance present in small quantity (A, see p. 1740).

From the concentrated filtrate, the new substance separates as a meal of short prisms (Found : N = 5·0. $C_{16}H_{15}O_4N$ requires N = 4·9 per cent.).

Anilino-m-*opianic acid* (formula XIII) melts at 213—214° and is very sparingly soluble even in boiling methyl alcohol; it dissolves more readily in acetone and crystallises well in short prisms.

It is coloured yellow by concentrated hydrochloric acid and dissolves in concentrated sulphuric acid, yielding a deep pure yellow solution which, on the addition of a drop of nitric acid, changes to intense brown. It is soluble in dilute ammonia in the cold to a colourless solution. The decomposition of this substance by hot dilute hydrochloric acid into aniline hydrochloride and m-opianic acid is described on p. 1740.

Action of p-*Toluidine on* 4 : 5-*Dimethoxyphthalonic Acid.*—The solution of the acid (2·5 grams) in boiling water (25 c.c.) was mixed with p-toluidine (3·5 grams) and the whole heated on the steam-bath, when a crystalline substance separated which was collected with the aid of the pump and washed first with water and then with light petroleum. The colourless residue of the p-*toluidine* salt of p-*toluidino*-4 : 5-*dimethoxyphthalonic acid* (compare p. 1727) separates from methyl alcohol in glistening flakes and decomposes, with evolution of gas, at 163—165° (Found : N = 6·3. $C_{25}H_{26}O_6N_2$ requires N = 6·2 per cent.). When this substance (3 grams) was boiled in a reflux apparatus with xylene (12 c.c.) for half an hour, crystals of p-*toluidino*-m-*opianic acid* (formula XIV) began to separate from the hot liquid. After cooling, the substance was collected and washed with benzene, when it melted at about 223° (Found : N = 4·7. $C_{17}H_{17}O_4N$ requires N = 4·7 per cent.).

This substance is decomposed on boiling with dilute hydrochloric acid in a similar manner to the corresponding anilino-derivative, yielding p-toluidine hydrochloride and m-opianic acid.

m-*Opianic Acid* (4 : 5-*Dimethoxy-o-aldehydobenzoic Acid*)
(Formula VII).

This acid may be obtained from 4 : 5-dimethoxyphthalonic acid (i) by boiling with a solution of sodium hydrogen sulphite, or (ii) by digesting anilino-m-opianic acid (see above) with dilute hydrochloric acid.

In process (i), the phthalonic acid (25 grams), dissolved in water and mixed with anhydrous sodium carbonate (11 grams), is evaporated to dryness, when the sodium salt remains as a satiny,

3 o*

crystalline mass. Freshly-prepared sodium hydrogen sulphite (100 c.c. of 50 per cent.) is warmed at 50°, the powdered sodium salt gradually added, and the whole heated in a water-bath at 60° for half an hour and then on the steam-bath until gas ceases to be evolved. The mass is evaporated to a paste, mixed with a large excess of 10 per cent. hydrochloric acid, evaporated to complete dryness, and extracted with ether in a Soxhlet apparatus for ten days, during which nearly pure *m*-opianic acid separates from the ether in crusts. The drawbacks to this process are the tedious ether extraction and the fact that the yield is not more than 60 per cent. of that theoretically possible.

In process (ii), crude anilino-*m*-opianic acid (as it separates from the xylene, p. 1738), in quantities of 10 grams, is heated on the steam-bath with water (50 c.c.) and concentrated hydrochloric acid (20 c.c.), when the yellow colour first produced soon fades and partial solution takes place. After half an hour, the whole is cooled, the precipitated acid collected, washed with a little water, warmed with dilute sodium carbonate solution, and filtered from a small quantity of an insoluble substance (A).* On acidifying the filtrate with hydrochloric acid, a chalky precipitate separates which melts at 184—185° and consists of almost pure *m*-opianic acid.

After recrystallisation from water, in which the acid is very sparingly soluble in the cold and from which it separates as a chalky powder consisting of microscopic, fern-like groups of needles, the melting point was 186—187° (Found : $C = 57.2$; $H = 5.0$. $C_{10}H_{10}O_5$ requires $C = 57.1$; $H = 4.8$ per cent.). *m*-Opianic acid is very sparingly soluble even in boiling methyl alcohol, but dissolves readily in boiling acetone ; it is also readily soluble in glacial acetic acid and separates in microscopic balls of needles. It crystallises particularly well from 50 per cent. acetic acid in rather characteristic stars of long, striated needles. A careful comparison showed that this acid is identical with the *m*-opianic acid (m. p. 184—185°) obtained from crypt⦿pidene by oxidation with permanganate (T., 1916, **109**, 928). In addition to the properties recorded at that time, the following observations have been made. A mixture of the acid with phenol gives, with a little concentrated sulphuric acid, a pale cherry-red coloration which, on warming,

* This curious substance is almost insoluble in the ordinary organic solvents, but crystallises from much boiling glacial acetic acid in lemon-yellow spangles which do not melt at 280° (Found : $C = 66.3$, 66.0 ; $H = 5.2$, 5.3 ; $N = 4.3$, 4.5. $C_{16}H_{15}O_4N$ requires $C = 67.4$; $H = 5.3$; $N = 4.9$ per cent.). This substance is insoluble in boiling methyl-alcoholic potassium hydroxide, but dissolves readily in concentrated sulphuric acid without change of colour, and the addition of water gives a gelatinous precipitate.

becomes deeper and then brown. Water precipitates a yellowish-green substance which dissolves in sodium hydroxide to a cherry-red solution. The acid, suspended in benzene containing thiophen, gives with sulphuric acid an intense cherry-red coloration which disappears on dilution with water. The acid dissolves in sulphuric acid to a yellow solution, which gradually becomes brown; at 160°, much sulphur dioxide is disengaged and the colour becomes deep green and then violet. On adding water, a brown substance separates which dissolves in sodium hydroxide, producing a deep violet solution, evidently due to the presence of an anthraquinone derivative corresponding with rufiopin (tetrahydroxyanthraquinone), which is formed under similar conditions from opianic acid (Liebermann and Chojnacki, *Annalen*, 1872, **162**, 323).

The Methyl Esters of m-*Opianic Acid* (compare p. 1728).

The *normal methyl* ester (formula IX) is obtained when methyl iodide reacts with the silver salt of *m*-opianic acid.

This silver salt was precipitated, on the addition of excess of silver nitrate to the neutral solution of the ammonium salt of *m*-opianic acid, as a gelatinous mass which, on standing and especially on warming, became granular and crystalline. It was collected with the aid of the pump, washed well, and dried on porous porcelain in the steam-oven (Found: $Ag = 34.0$. $C_{10}H_9O_5Ag$ requires $Ag = 34.0$ per cent.).

The dry salt was powdered, digested with anhydrous ether and excess of methyl iodide in a reflux apparatus for two hours, and the ethereal solution evaporated, when a colourless syrup remained which gradually crystallised in warty groups; crystallisation was much facilitated by rubbing with a little methyl alcohol. After draining on porous porcelain, the substance was recrystallised from methyl alcohol, in which it was much more readily soluble than the *pseudo*-methyl ester (see below) (Found: $C = 58.7$; $H = 5.2$. $C_{11}H_{12}O_5$ requires $C = 58.9$; $H = 5.3$ per cent.).

This *normal methyl* ester of m-*opianic* acid melts at 93—95° and is readily soluble in benzene and most organic solvents, but is sparingly soluble in light petroleum. It is insoluble in cold dilute sodium hydroxide, but dissolves readily on warming, and hydrochloric acid gives a precipitate of *m*-opianic acid melting at 185°.

Action of Aniline.—When aniline is added to the warm solution of the normal methyl ester in methyl alcohol, the clear liquid soon begins to deposit a colourless, crystalline substance which melts at about 143° (Found: $N = 4.8$. $C_{17}H_{17}O_4N$ requires $N = 4.7$ per cent.).

There can be no doubt that this interesting substance is the methyl ester of normal anilino-*m*-opianic acid,

$$(MeO)_2C_6H_2(CO_2Me)\cdot CH\colon N\cdot C_6H_5.$$
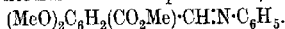
The *pseudo-methyl* ester of m-*opianic acid* (formula X) is produced when *m*-opianic acid (2·5 grams) is boiled with methyl alcohol (50 c.c.) in a reflux apparatus for two hours. The product is concentrated to a third of its bulk, when, on standing, the *pseudo-methyl* ester (2·2 grams) separates as a mass of colourless needles (Found : C = 59·0; H = 5·3. $C_{11}H_{12}O_5$ requires C = 58·9; H = 5·3 per cent.).

This pseudo-methyl ester melts at 142—143° and is less soluble in organic solvents than the normal methyl ester. It dissolves, however, readily in benzene, but is almost insoluble in light petroleum, and crystallises well from a mixture of benzene and a little light petroleum in needles. It does not dissolve in dilute methyl-alcoholic potassium hydroxide in the cold, but, on boiling, is at once converted into the sparingly soluble potassium salt of *m*-opianic acid. It differs from the normal methyl ester in crystallising unchanged from hot methyl alcohol to which aniline has been added.

Anhydride of m-*Opianic Acid.*

This substance is readily produced when the acid, contained in a test-tube, is heated in a sulphuric acid bath for four hours at 200° and then for two hours at 230°. The residue is pale brown and sets to a transparent mass like colophony, which is almost insoluble in water or dilute ammonia.

It was powdered, dissolved in boiling acetone, the solution digested with animal charcoal, and concentrated, when, on cooling, a voluminous mass of colourless needles separated (Found : C = 59·5; H = 4·5. $C_{20}H_{18}O_9$ requires C = 59·7; H = 4·5 per cent.).

This anhydride shrinks at 210° and melts at about 230°; it is sparingly soluble in cold methyl alcohol or acetic acid, but dissolves very readily in boiling acetone. It crystallises well from acetic acid as a voluminous mass of needles. It does not dissolve in methyl-alcoholic potassium hydroxide in the cold, but does so readily on warming and, after adding water and boiling away the methyl alcohol, the addition of hydrochloric acid gives a clear solution, from which *m*-opianic acid crystallises in needles melting at 185°.

Action of Aniline on m-*Opianic Acid.*

When the boiling aqueous solution of the acid is mixed with aniline, a cloudy liquid is produced and soon a mass of crystals will separate. The same substance is obtained when aniline is

added to a boiling methyl-alcoholic solution of *m*-opianic acid. It is sparingly soluble in boiling methyl alcohol and crystallises in stout prisms melting at 213—214°.

An analysis, careful comparison, and mixed melting-point determination showed that this substance is identical with the anilino-*m*-opianic acid obtained in the manner described on p. 1727. As this result was unexpected (compare p. 1729), a similar experiment was made on the action of *p*-toluidine on *m*-opianic acid, when a substance was immediately produced which, after crystallisation from methyl alcohol, melted at 220—222° and was found to be identical with the *p*-toluidino-*m*-opianic acid described on p. 1727.

Action of Phenylhydrazine on m-*Opianic Acid : Formation of the Phenylhydrazone of* m-*Opianic Acid and of Phenyl-*m-*opiazone* (Formulæ XVIII and XIX).

When phenylhydrazine is added to the boiling aqueous solution of *m*-opianic acid, a voluminous, crystalline precipitate separates which, since it is completely soluble in cold dilute ammonia, evidently consists entirely of the phenylhydrazone and does not contain any phenyl-*m*-opiazone (see below). This substance is very sparingly soluble in boiling methyl alcohol, and separates in minute, lemon-yellow needles which must be at once collected, because, if allowed to remain, they will become contaminated with colourless crystals of *phenyl-*m-*opiazone* (Found : $N = 9.2$. $C_{16}H_{16}O_4N_2$ requires $N = 9.3$ per cent.). The hydrazone shows a striking behaviour in a capillary tube, since at 185—190° the yellow crystals suddenly become colourless owing to conversion into phenyl-*m*-opiazone and the melting point is then 228°. Another way of converting the hydrazone into the opiazone is by boiling with concentrated hydrochloric acid, when the orange solution first produced becomes colourless and crystals of the opiazone separate. This substance was recrystallised from much alcohol, from which it separated in glistening needles melting at 228° (Found : $N = 9.8$. $C_{16}H_{14}O_3N_2$ requires $N = 9.9$ per cent.).

*Phenyl-*m-*opiazone* dissolves in concentrated sulphuric acid to a colourless solution, and the addition of a drop of nitric acid produces a salmon coloration which is discharged by water.

Action of as-*Phenylmethylhydrazine.*—When the boiling aqueous solution of *m*-opianic acid is mixed with phenylmethylhydrazine, a voluminous, crystalline precipitate separates which crystallises from alcohol, in which it is very sparingly soluble, in balls of yellow needles (Found : $N = 9.1$. $C_{17}H_{18}O_4N_2$ requires $N = 8.9$ per cent.). The *phenylmethylhydrazone* of *m*-*opianic acid* melts at about 237° without change of colour, and is incapable, owing to

the presence of the methyl group, of being converted into a substance of the type of phenyl-m-opiazone. When heated at $250°$, this substance melts to a dark brown syrup, gives off gas, and the residue crystallises in needles insoluble in ammonia. No further examination was, however, made of this product.

Action of Phenylhydrazine and of Phenylmethylhydrazine on Opianic Acid.

These experiments were instituted with the object of comparing the behaviour of opianic acid and m-opianic acid when treated with these reagents. Liebermann (*Ber.*, 1886, **19**, 764) states that the hot aqueous solution of opianic acid gives, with phenylhydrazine hydrochloride and sodium acetate, an oil which, on cooling, solidifies and after recrystallisation melts at 175° and has the formula $C_{16}H_{14}O_3N_2$ (phenylopiazone). Since this behaviour is very different from that of m-opianic acid (see above), the action of phenyl-hydrazine on opianic acid was repeated and it was found that the oil produced on mixing a hot aqueous solution of opianic acid with phenylhydrazine is evidently the normal phenylhydrazone, $C_{16}H_{16}O_4N_2$, since it is completely soluble in ammonia in the cold. This substance, unlike the phenylhydrazone of m-opianic acid, is very unstable and quickly passes into phenylopiazone with loss of water. The stable phenylmethylhydrazone is readily obtained when a boiling aqueous solution of opianic acid (5 grams) is mixed with phenylmethylhydrazine (2·5 c.c.). The milky liquid deposits an oil which will soon crystallise, and this substance separates from methyl alcohol, in which it is readily soluble, in groups of lemon-yellow needles (Found : N = 8·9. $C_{17}H_{18}O_4N_2$ requires N = 8·8 per cent.).

Opianic acid phenylmethylhydrazone melts at 167° with previous softening, and is immediately soluble in cold dilute ammonia.

THE DYSON PERRINS LABORATORY,
        OXFORD.   [*Received, September 27th*, 1921.]

CXCVIII.—The Constitution of Polysaccharides. Part III. The Relationship of 1-Glucosan to d-Glucose and to Cellulose.

By JAMES COLQUHOUN IRVINE and JOHN WALTER HYDE OLDHAM.

IN a previous communication (Irvine and Soutar, T., 1920, **117**, 1489) it has been shown that the yield of pure glucose obtainable

from cotton cellulose is, as a minimum, 85 per cent. of the theoretical amount calculated on the basis of the equation $(C_6H_{10}O_5)_n + nH_2O \longrightarrow nC_6H_{12}O_6$. This result is in itself insufficient to prove that the molecular unit of unmodified cellulose consists entirely of condensed glucose residues, but additional evidence pointing to this conclusion has been obtained in the course of recent work (Monier-Williams, this vol., p. 803). During the past four years, discussion on the constitution of cellulose has been prominent, and of the various structural alternatives which have been put forward the simplest is that cellulose may be regarded as a polymeride of $C_6H_{10}O_5$. The unit, in turn, would be derived from glucose, so that, on this basis, the degradation of cellulose involves both depolymerisation and hydrolysis. It is unnecessary to review the earlier literature in which this idea has been developed, as the subject has been extensively studied by Pictet and his collaborators who, in a series of papers, have contributed some interesting suggestions (Pictet and Sarasin, *Helv. Chim. Acta*, 1918, **1**, 187, and subsequent papers).

It will be recalled that, by subjecting either cellulose or starch to dry distillation under diminished pressure, Pictet obtained a number of volatile products, the most significant being the well-defined crystalline compound hitherto known as "*l*-glucosan." The compound in question, which had previously been obtained by the hydrolysis of certain natural glucosides, possesses the formula $C_6H_{10}O_5$ and is convertible into glucose on treatment with acids. Glucosan thus represents one of the possible anhydro-glucoses, and it may be remarked that according to current views on sugar structure (Irvine, Fyfe, and Hogg, T., 1915, **107**, 524, and subsequent papers) no fewer than forty non-reducing anhydro-glucoses may exist, and the number of isomerides is increased to 100 if reducing compounds are taken into account. Pictet's observation is interesting and offers a convenient method of preparing glucosan, but it is doubtful if the formation of this anhydride gives any clue to the constitution of starch or of cellulose. According to Pictet, both polysaccharides are polymerides of glucosan, and consequently dry distillation involves merely disruption of the complexes into the simple units of which they are composed. In the particular case of carbohydrates, where the complexity of the changes undergone during heating are notorious, it is unlikely that clear evidence as to molecular structure could be obtained in any reaction conducted at high temperatures. Nevertheless Pictet, in extending his experiments on the dry distillation of carbohydrates and their derivatives, has not only claimed that cellulose and starch are polymerides of glucosan, but has not hesitated to propose radical alterations in the formulæ generally accepted for certain natural

glucosides, the suggestions being based on the fact that, in such cases also, glucosan was present in the volatile products of decomposition. These conclusions will be criticised in due course, meanwhile it may be stated that the results now communicated show that there is no structural relationship between cellulose and l-glucosan. It is inadvisable to speculate as to the course of the reactions involved in the dry distillation of cellulose, but, as acids are produced, it is highly probable that hydrolysis to β-glucose is an essential factor and that the sugar is thereafter converted into the corresponding anhydride. It has, in fact, been proved experimentally in the course of the present research that l-glucosan is $1 : 6$-β-glucose anhydride and accordingly the expression " β-glucosan " may be substituted for the older name.

In order to explain the principle underlying the investigation, it is necessary to refer to results obtained in this laboratory by Denham and Woodhouse (T., 1913, **103**, 1735, and subsequent papers). These workers found that cellulose could be converted into a trimethyl cellulose from which, on hydrolysis, a crystalline trimethyl glucose was obtained. Obviously, if cellulose is a polymerised β-glucosan, trimethyl cellulose must be regarded as a polymeride of trimethyl β-glucosan. Pictet's views can thus be subjected to a rigid experimental test by preparing trimethyl glucosan and converting it into the corresponding trimethyl glucose by hydrolysis. The scheme involved, together with the relationship of cellulose to cellobiose, may be represented diagrammatically as under :
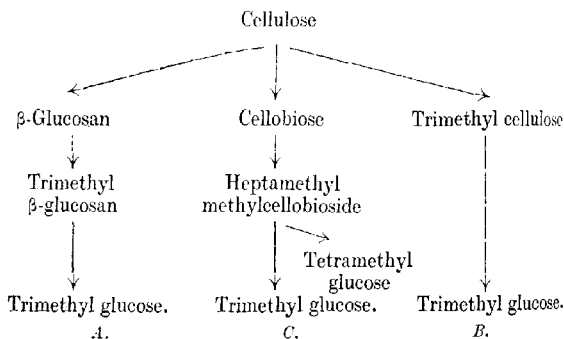
If the trimethyl glucoses indexed as A and B are identical, it follows that the glucosan unit is present in cellulose, and Pictet's polymerisation theory would then receive strong support. On the other hand, if the methylated glucoses are isomeric, Pictet's views cannot be

upheld. We find that the trimethyl glucose (A) derived from glucosan is not identical with that prepared from trimethyl cellulose, but is the sugar already obtained by one of us from methylglucoside (Irvine and Dick, T., 1919, **115**, 593) and by Haworth and Leitch (T., 1919, **115**, 809) from maltose. Further, the identity of B and C (Haworth and Hirst, this vol., p. 193) shows clearly that the cellobiose residue is an integral part of the cellulose molecule.

β-Glucosan, prepared by Pictet's method, was converted by the silver oxide reaction into trimethyl β-glucosan, at least two treatments with the methylating mixture being necessary. Unless properly conducted, excessive oxidation occurred with the consequent formation of alkylated acids and esters, but under suitable conditions a good yield of trimethyl glucosan was obtained. This compound distilled at 135°/12 mm. as a mobile, refractive liquid which solidified to a mass of large, colourless prisms, melting after recrystallisation from ethyl acetate or from ether at 63—64°. The compound is readily soluble in organic solvents, is lævorotatory, and is devoid of action upon Fehling's solution.

When trimethyl β-glucosan was heated at 100° with dilute hydrochloric acid, the rotation altered from lævo to dextro, and the trimethyl glucose thus produced was isolated as described in the experimental part. The properties of the sugar are compared below with those of the isomeride obtained from trimethyl cellulose.

Trimethyl glucose from glucosan.	*Trimethyl glucose from trimethyl cellulose.*
Liquid; b. p. 160—164°/0·2 mm.	Crystalline; m. p. 123—124°.
Gives trimethyl glucosan on heating.	Stable on heating.
Gives a crystalline β-methylglucoside.	Gives a liquid β-methylglucoside.
May be obtained from maltose but not from cellobiose.	May be obtained from cellobiose but not from maltose.

Despite the fact that their optical rotations lie close together, there can be no doubt that the compounds are utterly distinct, and the significance of this result has already been pointed out.

With the object of establishing the constitution of glucosan, attention was accordingly directed to the detailed study of the trimethyl glucose obtained from it. The variable optical rotations displayed by different preparations of the sugar suggested its identity with the form of trimethyl glucose already isolated from methylglucoside and from maltose.

Trimethyl Glucose.

	(1) From methyl-glucoside.	(2) From maltose.	(3) From β-glucosan.
$[\alpha]_D$ in water	+ 48·6°; 60·7°	+ 69·3°	+ 47·3°; 66·8°
,, in acetone	+ 46·2°; 58·8°	+ 61·4°	+ 60·8°
n_D	1·4780 1·4768	1·4792	1·4780; 1·4789
Composition found	C = 49·03;	C = 48·52;	C = 48·58;
	H = 7·98	H = 8·02	H = 8·09

Composition calculated ... C = 48·64; H = 8·10 %.

It will be seen that although the five different preparations of the sugar proved on oxidation to be identical in structure, the specific rotations showed curious irregularities. A satisfactory explanation of this is found in the analytical results, in which the hydrogen value is slightly low whilst the carbon content is either very close to the calculated value or is actually higher. We have shown that the variations in activity and the abnormality in the analytical results are due to the tendency of the sugar to pass into the corresponding anhydride, small quantities of which are produced in the course of vacuum distillation. This internal dehydration takes place most readily with the β-isomeride and the production of even minute quantities of the β-anhydride (that is, trimethyl glucosan) depresses the activity greatly without notable alteration of the analytical results.

The most trustworthy optical rotation of the trimethyl glucose is given by observing the end-point attained when the sugar is formed by hydrolysis. Thus, on hydrolysing trimethyl glucosan, the specific rotation of the sugar present in the solution was +75·8°, whilst starting from trimethyl methylglucoside the value +73·8° was recorded. The true rotation of the sugar in water is doubtless of the above order, but the identification of this form of trimethyl glucose is a difficult matter and depends ultimately on the results of oxidation.

In the first place, in order to establish that the trimethyl glucose obtained from glucosan is a derivative of butylene-oxide glucose, the compound was fully methylated by the silver oxide reaction. The product consisted of α- and β-tetramethyl methylglucosides which, on hydrolysis, were converted into tetramethyl glucose of the butylene-oxide type, melting, after recrystallisation, at 95—96°.*

* It is unfortunately necessary to correct one of the misleading statements made by Karrer, who has chosen to conduct investigations on the field associated with this laboratory and to copy our methods. He claims (Karrer

When oxidised with nitric acid, the trimethyl glucose was converted into trimethyl saccharolactone, which was isolated in the form of its ethyl ester. From this, in turn, the parent lactonic acid was regenerated and found to be identical with that described by Haworth and Leitch (*loc. cit.*). The compound is thus derived from a dibasic acid, and the trimethyl glucose yielding such an acid must have the constitution shown below :

$$\overset{\overline{} O \overline{}}{OH \cdot CH_2 \cdot CH(OMe) \cdot CH \cdot CH(OMe) \cdot CH(OMe) \cdot CH \cdot OH.}$$
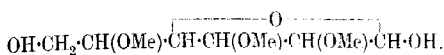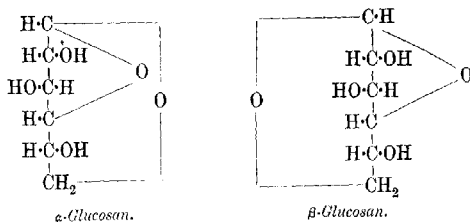
As a necessary consequence, it follows that in the formation of glucosan from glucose, dehydration involves the reducing group and also the terminal primary alcoholic group. Provided the butylene-oxide structure is preserved (which has now been shown to be the case), two possibilities are available according as the sugar reacts in its α- or β-form. There should thus be two possible glucosans possessing the following constitution :

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and Widmer, *Helv. Chim. Acta*, 1921, **4**, 174) that " β-tetramethyl glucose " melts at 94°, and not at the lower values which have been reported in our papers. It may be pointed out that although many researches have been devoted to the subject, β-tetramethyl glucose is quite unknown, as only the α-form and the equilibrium mixture have been isolated. Evidently Karrer has made the elementary mistake of assuming that a sugar isolated from a β-glucoside will permanently retain the β-configuration.

That Karrer's statement is not due to a typographical error is confirmed by the importance he attaches to the fact that, in the complete methylation of cellobiose, he obtained a pure β-form, whereas Haworth and Hirst's preparation of heptamethyl methylcellobioside (*loc. cit.*) admittedly contained some of the α-isomeride. This implied criticism of Haworth and Hirst's results is quite unjustified, as, irrespective of the proportions of α- and β-forms in a glucoside, the same sugar is isolated after hydrolysis. This was established many years ago (Purdie and Irvine, T., 1904, **85**, 1049, and subsequent papers) as part of the pioneer work conducted in this laboratory in preparation for our investigation of the constitutional problems of the di- and poly-saccharides.

The error made by Karrer is unlikely to mislead experienced workers in the sugar group, but unless corrected may give rise to confusion in view of the complications of the nomenclature now in use.

Further, it must be stated that it has long been known to us that the melting point of tetramethyl glucose rises as the content of the α-isomeride increases. The melting point thus varies greatly according to the proportion of α-form present and is further affected, owing to conversion into the β-isomeride, by the rate of heating during the determination. Values of 100° may be obtained by rapid heating, but we prefer to quote an average figure based, not on one result, but on an experience extending over twenty years.
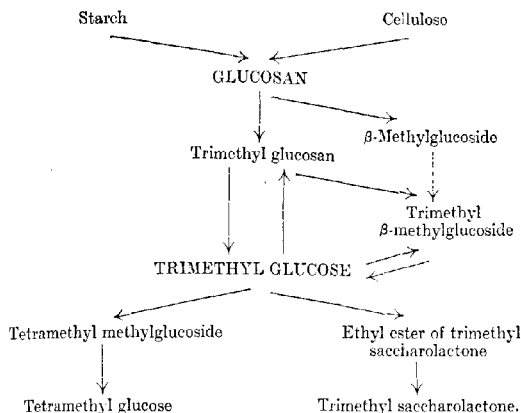
$$\begin{array}{c}
\text{H·C} \\
\text{H·C·OH} \\
\text{HO·C·H} \\
\text{H·C} \\
\text{H·C·OH} \\
\text{CH}_2
\end{array} \quad O$$

$$\begin{array}{c}
\text{C·H} \\
\text{H·C·OH} \\
\text{HO·C·H} \\
\text{H·C} \\
\text{H·C·OH} \\
\text{CH}_2
\end{array} \quad O$$

α-*Glucosan.*   β-*Glucosan.*

The above formulæ are based on Böeseken's structure for α- and β-glucose, and lead at once to the conclusion that lævo-glucosan is derived from β-glucose. This agrees with the formula put forward by Pictet (*Helv. Chim. Acta*, 1920, **5**, 649) and the β-configuration was confirmed in the following way. β-Glucosan was heated at 100° with methyl alcohol containing 0·5 per cent. of hydrogen chloride, the time of treatment being varied so as to arrest the reaction before the methylglucoside first formed had assumed equilibrium with its stereoisomeride. The crystalline product invariably contained a greater proportion of the β-isomeride than was found in the equilibrium mixture by Jungius (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, **6**, 99), thus indicating that β-methylglucoside is the first product when the glucosan ring is opened.

Parallel experiments conducted on trimethyl glucosan gave a similar result, and the reaction yielded mainly the crystalline trimethyl β-methylglucoside, m. p. 86—88°. As this particular glucoside had not been previously obtained in the β-form, the compound was prepared directly from trimethyl glucose. The two preparations proved to be identical in every respect, thus confirming the β-configuration of lævo-glucosan.

It is now possible to trace the main reactions which are responsible for the formation of β-glucosan from cellulose. In the course of the dry distillation, acids are produced in considerable quantity with the consequent formation of glucose. The β-form of the sugar then undergoes dehydration and distils forward as the anhydride. It may be remarked that the distillation under diminished pressure of carbohydrates and their derivatives is greatly affected by the speed of heating. When the time of contact with the hot surface is reduced to a minimum it is possible to remove the volatilised material before appreciable decomposition takes place. Thus, we find that, under conditions described in the experimental part, not only β-glucosan but both α- and β-methylglucosides may be distilled unchanged in practically quantitative amount. These examples show that many factors are operative in determining when a carbohydrate or its derivatives

may be found in the products of dry distillation, but it is evident that any compound which yields β-glucose on hydrolysis may be expected to yield β-glucosan in Pictet's reaction. The complete series of reactions carried out in the course of the research is shown in the following scheme :

Starch   Celluloso

GLUCOSAN

β-Methylglucoside

Trimethyl glucosan

Trimethyl
β-methylglucoside

TRIMETHYL GLUCOSE

Tetramethyl methylglucoside   Ethyl ester of trimethyl
                                                    saccharolactone

Tetramethyl glucose   Trimethyl saccharolactone.

Discussion of Results.

The essential point which has emerged as an issue of the present research is that β-glucosan bears no structural relationship to cellulose. Pictet's views appear to have been widely accepted, but have not escaped criticism, and, in particular, it has been pointed out that they are inconsistent with the fact that cellulose can be degraded to cellobiose, and starch to maltose. It has now been established that the conversion of cellulose into β-glucosan is essentially a dry distillation of β-glucose. Our results thus support the opinion expressed by Hess and Mittelsbach (*Zeitsch. Elektrochem.*, 1921, **26**, 232) and no other conclusion can be drawn than that the production of glucosan from cellulose is adventitious.

Recently, however, Reilly (*Helv. Chim. Acta*, 1921, **4**, 616) has replied to Hess and produced evidence which he claims to substantiate Pictet's polymerisation theory. Reilly subjected methylated celluloses to dry distillation under diminished pressure and obtained a " dimethyl lævo-glucosan " from which a " dimethyl glucose " was obtained. These results have no bearing on the problem at issue. An incompletely methylated cellulose, irrespective of its constitution, would give products of the above
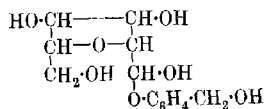
composition, and the conversion of the dimethyl glucose into a trimethyl glucose which could be compared with Denham and Woodhouse's product would be valueless (even if it were possible), as there is no means of determining which of the hydroxyl positions available for methylation should be substituted. The results we now contribute supply the necessary information and lead to an entirely different conclusion.

With regard to the structure of β-glucosan, the formula we suggest agrees with that which Pictet finally supported (*Helv. Chim. Acta,* 1920, **3**, 649), but it must be pointed out that his explanation of the isomerism displayed by the so-called " *d-* " and " *l-* " glucosans is most improbable. He regards both anhydrides as derived from the same form of glucose, the anhydride ring being an ethylene oxide for the *d*-form, and a hexylene oxide for the *l*-isomeride. In all probability *d*-glucosan will be found to be an anhydride of α-glucose just as *l*-glucosan is now shown to be the 1 : 6-anhydride of β-glucose.

Suggested Relationship of β-Glucosan to Natural Glucosides.

In developing the idea that β-glucosan is a constituent part of important carbohydrates, Pictet (*Helv. Chim. Acta,* 1919, **2**, 698) has proposed radical alterations in the constitution of certain natural glucosides. Recognising that many of these compounds share with β-glucosan the property of being lævorotatory, he suggests that they are structurally related. So many objections may be offered to this opinion that it is needless to summarise them. The fact that typical glucosides, such as salicin, give β-glucosan on dry distillation is regarded by Pictet as confirmatory evidence, but if reference to the standard literature on the sugars is made it is inconceivable that such views will find acceptance. Natural glucosides are lævorotatory in that essentially they are derivatives of β-glucose, and it may be recalled that when Nef put forward the idea that α- and β-glucosides differed structurally, and not in the stereochemical position of the glucosidic group, his arguments were convincingly refuted by Fischer.

One of the test cases quoted by Pictet may now be criticised in detail in order to show how divergent his glucoside formula is from well-established reactions. He suggests for salicin the structure

$$
\begin{array}{l}
\text{HO·CH}\!-\!\!-\!\!-\!\text{CH·OH} \\
\quad\text{CH}\!-\!\text{O}\!-\!\text{CH} \\
\quad\text{CH}_2\text{·OH} \quad \text{CH·OH} \\
\qquad\qquad\quad \text{O·C}_6\text{H}_4\text{·CH}_2\text{·OH}
\end{array}
$$

Quite apart from the fact that a substance of the above type would probably be a reducing sugar and not a glucoside, it is evident that no attention has been directed to the constitutional study of salicin undertaken by Irvine and Rose (T., 1906, **89**, 814). These workers prepared, both synthetically and directly from salicin, a well-defined, crystalline pentamethyl salicin. This, in turn, gave on hydrolysis tetramethyl glucose of the butylene-oxide type :

$$\overset{\overbrace{\hspace{3cm}}O\hspace{3cm}}{OMe{\cdot}CH_2{\cdot}CH(OMe){\cdot}CH{\cdot}CH(OMe){\cdot}CH(OMe){\cdot}CH{\cdot}OH} \cdot$$
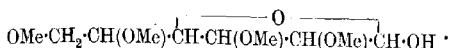
In other words, salicin is constituted on the same model as β-methyl-glucoside, so far as the sugar chain is concerned.

On the other hand, according to Pictet's formula the only alkylated sugar obtainable from pentamethyl salicin would be a tetramethyl hexose of the structure shown below :

$$OMe{\cdot}CH_2{\cdot}\underset{\underbrace{\hspace{2.5cm}}O}{CH{\cdot}CH(OMe){\cdot}CH(OMe){\cdot}C(OH){\cdot}CH_2{\cdot}OMe.}$$
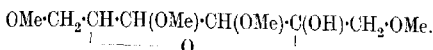
The above sugar has already been described and is not a derivative of glucose, but is the tetramethyl fructose of the butylene-oxide type (Steele, T., 1918, **113**, 257). It bears no relationship to tetramethyl glucose, which, as stated, has long been known to result when pentamethyl salicin is hydrolysed.

The acceptance of Pictet's views would thus mean that the naturally-occurring glucosides showing a lævorotation are not glucosides but fructosides. It may be remarked that, since putting forward his glucoside formula, Pictet has revised his opinion as to the constitution of glucosan. He has not, however, corrected his formulæ for salicin and other natural glucosides, nor would it be possible to do so without assuming rupture of the butylene oxide ring. This again would preclude the possibility of pentamethyl salicin yielding tetramethyl glucose or of being synthesised from this sugar.

These criticisms are offered in the hope that the permanent literature of the sugars will not be further complicated by speculations on structure which are based on insecure evidence and are made without reference to previous work.

EXPERIMENTAL.

Preparation of β-Glucosan.

The conditions laid down by Pictet and Sarasin were followed and in the first instance a specially pure form of fibrous cellulose was employed. From the semi-crystalline distillate pure β-glucosan

was isolated, and similar results were obtained with cotton wool and filter paper. The use of cellulose in any form is inconvenient. The low thermal conductivity of the material prevents uniform heating of the mass and although in small-scale working the yield of distillate quoted by Pictet (44 per cent. of the cellulose taken) was verified, it was seriously diminished when larger quantities were employed. The bulk of the glucosan required was therefore prepared from starch, used in the form of lumps as the powdered material proved unsuitable owing to the fine particles being carried forward mechanically during the vacuum distillation.

The distillation apparatus was made of quartz and was attached to an efficient condensing system, the vacuum being provided by a Geryk oil pump driven electrically at a speed which kept the pressure at 8—10 mm. In the earlier experiments, heating was effected by immersion in a bath of fusible metal, but in large-scale working superior yields were obtained by heating with the free flame. This must be conducted cautiously at first, as otherwise the starch swells and fills the side tube of the flask, but in the later stages of the distillation both the bottom and sides of the flask were heated with powerful burners so as to prevent refluxing.

In each experiment 100 grams of starch were used, giving from 43—48 grams of a dark, viscous syrup which distilled at 250—300°/10 mm., a carbonaceous residue remaining behind. The syrup, on keeping in shallow vessels, gradually crystallised, and after draining on a porous plate the material was washed with cold acetone and crystallised from boiling alcohol. Thereafter, the product was decolorised by boiling in aqueous solution with animal charcoal and, on recrystallisation from water, gave pure β-glucosan. In all, 4300 grams of starch yielded 1670 grams of syrup, from which 230 grams of pure glucosan were isolated. The yield is thus less than 6 per cent. of the polysaccharide used, but may be much improved by modifications which will be described in another communication.

Preparation of Trimethyl β-Glucosan.

This reaction was carried out on several occasions, but only one typical experiment need be quoted. Twenty-five grams (1 mol.) of glucosan were dissolved in 132 grams (6 mols.) of methyl iodide mixed with 115 c.c. of methyl alcohol. Methylation was effected by the gradual addition of 108 grams (3 mols.) of silver oxide and the reaction was continued at the boiling point of the liquid for seven hours. On isolating the product in the usual manner, a viscous syrup remained which, as a rule, was fully soluble in methyl

iodide. Complete methylation resulted when a second treatment with the above proportions of the methylating reagents was given, very little, if any, extraneous solvent being employed. The product was extracted with boiling ether and the filtered extract dried and evaporated. In this way 27 grams of a mobile syrup remained which boiled indefinitely at 140—170°/20 mm. On repeated fractionation, the material was separated into two components, the main fraction boiling at 145—150°/18 mm. and the less volatile liquid at 165—169°/17 mm. The distillate of lower boiling point crystallised readily, and the solid was removed by suction and recrystallised from ether. The product separated in aggregates of rhombohedra, and an average specimen melted at 62°, the maximum recorded being 66°. The boiling point of the purified material was 135·5°/12 mm. (Found: C = 52·76; H = 7·75; OMe = 45·5. $C_9H_{16}O_5$ requires C = 52·94; H = 7·84; OMe = 45·6 per cent.). The molecular weight, determined in benzene by the ebullioscopic method, was 212 ($C_9H_{16}O_5$ requires M = 204), so that the compound was monomolecular.

Solvent.	c.	$[\alpha]_D^{20°}$.
Acetone	5·0000	— 63·6°
Water	5·0000	— 63·5
Methyl alcohol	4·9916	— 53·2
Benzene	5·0000	— 48·5

Conversion of Trimethyl β-Glucosan into Trimethyl Glucose.

A 7·5 per cent. solution of trimethyl glucosan was prepared in water containing 3·6 per cent. of hydrochloric acid and the solution was heated on a boiling-water bath, polarimetric readings being taken at intervals of an hour. The rotation gradually altered from lævo to dextro, and finally, after six to eight hours, attained a permanent value which varied between + 70·0° and 76·6°. Thereafter the acid was neutralised with lead or barium carbonate, and the solution filtered and evaporated to dryness in a vacuum. On extracting the residue with acetone and removing the solvent, a syrup remained. This was essentially trimethyl glucose contaminated with traces of lead compounds which were, however, left undissolved on extraction with ether. The purified sugar was distilled (b. p. 160—164°/0·2 mm.) and rectified in the course of a second distillation. The refractive index, n_D, was 1·4780 (Found: C = 48·58; H = 8·09; OMe = 41·9; M, in boiling benzene solution, = 231. $C_9H_{18}O_6$ requires C = 48·64; H = 8·10; OMe = 41·9 per cent.; M = 222).

The sugar was a colourless viscid syrup which showed no tendency to solidify when nucleated with the crystalline trimethyl glucose

prepared from cellulose. It failed to form an osazone and yielded a crystalline anilide only with difficulty, but gave a well-defined crystalline glucoside when condensed with methyl alcohol.

The following observations were made on the optical activity of the sugar :

Solvent.	c.	$[\alpha]_{D}^{20^{\circ}}$ varied from
Water	4·086	+ 42·7° to 66·8
,, ...	2·276	+ 47·3 --
Acetone	3·400	+ 60·8 to 70·5
Methyl alcohol	3·366	+ 55·6 to 69·1

As explained in the introduction, different preparations of this sugar give widely divergent specific rotations, and the values quoted above are the extremes found by us. Repeated distillation depressed the dextrorotation, lowered the hydrogen value, and increased the carbon content, so that the result is evidently due to dehydration and reconversion into trimethyl glucosan.

This was confirmed by heating a specimen showing the specific rotation + 45·9° with 6 per cent. hydrochloric acid. The dextro-rotation then increased rapidly and on again isolating the sugar it gave $[\alpha]_{D}$ + 62·2° in aqueous solution.

Constitution of the Trimethyl Glucose obtained from Trimethyl Glucosan.

Conversion into Tetramethyl Glucose.

Two methylations by means of the silver oxide reaction gave tetramethyl methylglucoside ($n_{D} = 1·4469$). This was hydrolysed in the usual manner and as the preparation was a mixture of α- and β-isomerides the rotation showed the customary rise and fall in the dextro-sense. The tetramethyl glucose thus produced melted at 96°, gave satisfactory analytical figures, and showed mutarotation in absolute alcohol ($[\alpha]_{D} + 99·4° \longrightarrow 84·3°$). In water, the optical change was $[\alpha]_{D} + 92·2° \longrightarrow 83·8°$, and these values agree well with the standards for tetramethyl glucose.

Oxidation of Trimethyl Glucose.

In order to decide which of the two possible trimethyl glucoses was present the sugar was oxidised in the usual manner with nitric acid (D 1·2). A variation was, however, introduced in that after the removal of the bulk of the nitric acid by successive concentration to half bulk at 40°/20 mm., alcohol was added and the evaporation repeated. This treatment was continued and the product was finally heated in absolute alcohol containing a trace of hydrogen

chloride. In this way the sugar was converted into the ethyl ester of trimethyl saccharolactone, which was purified by distillation under 0.4 mm. pressure (Found : C = 50.33; H = 6.78; OMe = 35.2; OEt = 17.03. $C_{11}H_{18}O_7$ requires C = 50.38; H = 6.87; OMe = 35.5; OEt = 17.2 per cent.). The compound was a pale yellow, mobile liquid and contained one lactonic and one esteric group (0.2005 gram required 12.55 c.c. of $N/10$-alkali in place of the calculated amount, 12.75 c.c.). Moreover, when dissolved in aqueous alcohol, the compound showed the decrease in dextro-rotation characteristic of lactones in this series.

Solvent.	c.	$[\alpha]_D^{20}$.
Absolute alcohol	1.016	+ 73.4°
50% Aqueous alcohol	1.106	+ 65.8° ⟶ 41.6° in seventy hours.

The ester was thereafter converted into the corresponding acid by heating in aqueous alcoholic solution with excess of barium hydroxide. After one hour at 100°, the excess of alkali was precipitated with carbon dioxide and the filtered liquid evaporated at 50°/20 mm. The barium salt thus obtained was decomposed with sulphuric acid and the lactonic acid isolated in the usual manner (Found : C = 46.02; H = 6.24; OMe = 38.9. $C_9H_{14}O_7$ requires C = 46.15; H = 5.98; OMe = 39.7 per cent.). The presence of one carboxyl and one lactonic group was confirmed by titration, and the change in specific rotation in 50 per cent. aqueous alcohol was + 76.1° ⟶ 54.8°. These constants are in good agreement with those previously determined for trimethyl saccharolactone.

Conversion of β-Glucosan into β-Methylglucoside.

For reasons given in the introduction, β-glucosan was converted into the corresponding methylglucoside under conditions which minimised the interconversion of the α- and β-forms. A 10 per cent. solution of β-glucosan in methyl alcohol containing 0.468 per cent. of hydrogen chloride was heated at 100°, and samples were abstracted at intervals in order to ascertain by methoxyl estimations when the whole of the glucosan had reacted. In this way it was possible to arrest the condensation before the glucosides had attained equilibrium. After forty-one hours' treatment, the crystalline product was isolated and found to consist of a mixture of the isomeric methylglucosides (Found : OMe = 15.2. $C_7H_{14}O_6$ requires OMe = 15.9 per cent.). The amount of pure β-methyl-glucoside present was 30 per cent., in place of 23 per cent., which is the proportion in equilibrium with the α-form. β-Methylglucoside is therefore the first to be produced when β-glucosan condenses

with methyl alcohol, thus proving the β-configuration of the anhydro-compound.

This was confirmed in the course of several experiments. For example, the reaction between glucosan and methyl alcohol was arrested when the specific rotation was $+72 \cdot 3°$. The mixed glucosides thereafter isolated consisted of $62 \cdot 0$ per cent. of the α- and 38 per cent. of the β-form. On continuing the condensation the proportion of the α-isomeride increased at the expense of the β-form, and this increase of activity at the end of the reaction confirms that β-methylglucoside is the first product of the condensation.

Conversion of Trimethyl β-Glucosan into Trimethyl β-Methylglucoside.

A $4 \cdot 4$ per cent. solution of trimethyl glucosan in methyl alcohol, containing $0 \cdot 5$ per cent. of hydrogen chloride, was heated at $110°$, and samples were withdrawn after the reaction had proceeded for eighty-five hours, one hundred and sixty-six hours, and one hundred and ninety hours respectively. In each case the products were isolated by standard methods and proved to be mixtures of the α- and β-isomeric forms of trimethyl methylglucoside. The β-compound, which crystallised on keeping, was separated by draining on a tile and purified from light petroleum. The compound was deposited in fine needles, m. p. 93—94° (Found : $C = 50 \cdot 78$; $H = 8 \cdot 57$; OMe = $50 \cdot 9$. $C_{10}H_{20}O_6$ requires $C = 50 \cdot 84$; $H = 8 \cdot 47$; OMe = $52 \cdot 5$ per cent.). For $c = 1 \cdot 5$, the specific rotation in methyl alcohol was $- 22 \cdot 9°$. When hydrolysed with $2 \cdot 5$ per cent. hydrochloric acid at $100°$, the compound was converted into trimethyl glucose, the specific rotation then altering from $- 19 \cdot 6°$ to $+ 69 \cdot 5°$ (corrected for the hexose formed, $+ 73 \cdot 8°$).

The liquid form of trimethyl methylglucoside consisted of the α-isomeride retaining some of the β-form in solution. This was shown by the behaviour on hydrolysis with $2 \cdot 5$ per cent. hydrochloric acid. The specific rotation then displayed the characteristic rise and fall significant of the presence of two isomerides of opposite rotation which hydrolyse at different speeds.

Time from start in minutes.	Specific rotation.
0	$+69 \cdot 7°$
60	$83 \cdot 6$
120	$80 \cdot 0$
380	$71 \cdot 3$

In this case also, clear evidence was obtained that the reaction of the methylated glucosan with methyl alcohol gave the corresponding β-glucoside in the first instance, as the proportion of the

crystalline isomeride steadily diminished with continued heating. Thus, when the condensation was arrested at the end of one hundred and sixty-six hours, the specific rotation of the liquid was $+ 55.6°$. After an additional twenty-four hours' heating, the value had increased to $+ 104.8°$ without any alteration in methoxyl content, showing that the final change is the conversion $\beta \longrightarrow \alpha$.

Distillation of β-Glucosan and of α- and β-Methylglucoside.

In view of the opinions expressed in the course of this paper, it was desirable to ascertain the behaviour of β-glucosan when heated under diminished pressure. It was found that when small quantities are used the compound may be distilled unchanged. 2·6 Grams of glucosan were heated in a silica flask connected by a short air-condenser to a receiver which was coupled to a pump. The material was heated with the naked flame. The compound melted and, under a pressure of 9 mm., commenced to sublime, but as the temperature was raised, normal distillation took place and 2·3 grams passed into the condenser and receiver. The product, after recrystallisation from alcohol, was pure β-glucosan, melting at 178—180° and showing $[\alpha]_D - 65.4°$ in aqueous solution.

α-Methylglucoside behaved similarly when heated in small quantities. Thus, 1·4 grams gave 1·3 grams of distillate which solidified to a glass on cooling. On crystallising from alcohol, this material was shown to be pure α-methylglucoside, melting at 167° and giving $[\alpha]_D + 155°$ in water.

β-Methylglucoside gave an equally satisfactory result and the distillate crystallised in the receiver. Without further purification the compound then melted at 104—106°, and this value was unaffected by crystallisation from ethyl alcohol or by admixture with an authentic specimen. The specific rotation in water was $- 30.0°$, and the distillate thus consisted of pure β-methylglucoside. The above result was not obtained when a metal bath was used as the source of heat, the glucosides then decomposing without distillation.

CXCIX.—*Studies in Emulsions. Part III. Further Investigations on the Reversal of Type by Electrolytes.*

By SHANTI SWARUPA BHATNAGAR.

IN a previous paper of this series (this vol., p. 61), the effects of a large number of electrolytes on the reversal of phases in emulsions prepared with univalent soaps have been described. A complete quantitative investigation on the effects of electrolytes on emulsion equilibrium being of fundamental importance for the elucidation of the mechanism of emulsification, attempts were made to examine whether emulsions prepared with the so-called insoluble emulsifiers of Pickering could undergo a reversal of type under the influence of electrolytes. The effects of volume ratio of the phases and temperature were minimised by carrying out the experiments at about 17—19° and by adding a moderate amount of the emulsifying agent to equal volumes of the two phases. It has been shown that under these conditions (Clayton, " Margarine Manufacture "; Bhatnagar, T., 1920, **117**, 542) the type of emulsion obtained is mainly dependent on the nature of the emulsifying agent. The emulsions were prepared in the manner described in previous papers (*loc. cit.*), and were examined by the drop method of Briggs and confirmed by the electrical method (*loc. cit.*) and under the microscope.

EXPERIMENTAL.

Finely-divided solids like basic salts of copper and nickel were first used by Pickering (T., 1907, **91**, 2002) in preparing concentrated emulsions. No attempts seem to have been made by him or any other investigator in the field to examine whether a reversal of type can be brought about in emulsions prepared in that fashion. Earlier attempts with ordinary, finely-powdered hydroxides of zinc, cadmium, and aluminium brought out nothing new. Later, it was considered desirable to prepare fresh samples of zinc hydroxide for use as emulsifying agent. In order to do so, about 6 grams of pure zinc sulphate were dissolved in about 200 c.c. of water and an excess of potassium hydroxide solution was added, so that all the zinc hydroxide precipitated was dissolved. Small quantities of dilute hydrochloric acid were then slowly added until the precipitate just reappeared. Such a solution, when kept for some time, threw down a moderately large quantity of zinc hydroxide as

coagulum. The coagulum and liquid were transferred to a parchment dialyser and left there for five days. The water in the outer vessel was changed from time to time until no more alkali diffused out through the dialyser and the liquid became neutral to litmus. The coagulum was then made up to a litre and transferred to a carefully cleansed, resistance-glass flask. On agitating this suspension with B.P. paraffin or kerosene oil, it was possible to form stable emulsions sensitive to electrolytes, the emulsions prepared by using the alkali-free suspensions of zinc hydroxide forming the water-in-oil type of emulsion, as opposed to those prepared by alkaline zinc hydroxide, which formed the oil-in-water type. The zinc hydroxide coagulum formed by precipitation with ammonia gave similar results in dialysed and undialysed forms as long as the coagulum was kept moist. Dried zinc hydroxide was incapable of forming stable emulsions. Several samples of 20 c.c. of suspension, each of equal weight, were emulsified with 20 c.c. of oil. The quantity of zinc hydroxide in the aqueous phase was approximately 3·2 grams per litre in each case. The effects of various electrolytes were then examined on emulsions prepared by using this suspension alone and with various electrolytes, and some of these results are shown in Table I.

TABLE I.

Zinc Hydroxide.

Amount of aqueous phase = 20 c.c.
Amount of kerosene oil = 20 c.c.
Quantity of zinc hydroxide = 3·2 grams per litre.

Electrolyte.		Quantity in gram-mols. per cent.	Type of emulsion.	Stability.
KCl	1	0·0005	W in O	
	2	0·001	,,	
	3	0·005	,,	
K₂SO₄	1	0·0005	,,	
	2	0·001	,,	All quite stable.
	3	0·006	,,	
Al₂(SO₄)₃	1	0·0001	,,	
	2	0·001	,,	
	3	0·005	,,	
K₂PO₄	1	0·001	,,	
	2	0·002		Separation into layers.
	3	0·003	O in W	
KOH	1	0·001	W in O	
	2	0·0015	O in W	
	3	0·002	,,	
NaOH		0·002	,,	

In order to obtain further results, coagula of lead oxide, lead carbonate, copper and aluminium hydroxides, casein, lecithin, rosin, and egg-albumin were prepared in a somewhat similar fashion, and some of them are described in detail later on.

Lead Oxide.

Preparation.—By precipitating the insoluble oxide by the action of the hydroxide on a solution of lead nitrate and dialysing the coagulum as in the case of zinc hydroxide.

TABLE II.

Amount of aqueous phase = 15 c.c.
Amount of oil phase — 15 c.c.
Amount of lead oxide = about 4·2 grams per litre.

Electrolyte.		Quantity in gram-mols. per cent.	Type of emulsion.	Stability.
KCl	1	0·002	W in O	
	2	0·004	,,	
	3	0·005	,,	Not very stable.
K₂SO₄	1	0·003	,,	
	2	0·0042	,,	
	3	0·006	,,	
Al₂(SO₄)₃	1	0·001	,,	
	2	0·003	,,	
	3	0·006	,,	
K₃PO₄	1	0·0021	,,	
	2	0·008	O in W	
	3	0·009	,,	
KOH	1	0·002	W in O	
	2	0·004	O in W	Stable in all other cases
	3	0·005	,,	

Aluminium Hydroxide.

The aluminium hydroxide was prepared by the action of ammonium hydroxide on a solution of pure aluminium sulphate. The moist precipitate was dialysed in parchment until the internal and the external water was neutral to litmus. This coagulum was made up to a litre and used as described in the case of zinc hydroxide. Some of the results are shown in Table III.

TABLE III.

Amount of aqueous phase = 20 c.c.
Amount of oil phase = 20 c.c.
Amount of aluminium hydroxide = about 3·8 grams per litre.

Electrolyte.		Quantity in gram-mols. per cent.	Type of emulsion.	Stability.
KCl	1	0·002	W in O	Not very stable.
	2	0·004	,,	,,
	3	0·005	,,	,,
K₂SO₄	1	0·002	,,	,,
	2	0·003	,,	,,
	3	0·005	,,	,,
K₂PO₄	1	0·001	,,	
	2	0·0035	—	Tendency to separate into two layers.
	3	0·004	O in W	Stable.
KOH	1	0·001	—	Tendency to separate.
	2	0·0015	O in W	Stable.
	3	0·002	,,	,,

Casein.

The casein was a pure sample supplied by Messrs. Baird and Tatlock. A weighed quantity was dissolved in $N/10$-potassium hydroxide and gradually precipitated by acetic acid, the coagulum being then dialysed as in previous cases. The results obtained by casein suspensions when the casein was used dry and when precipitated as described were very nearly identical and therefore the results with the former alone are given.

TABLE IV.

Amount of aqueous phase = 20 c.c.
Amount of oil phase = 20 c.c.
Amount of casein per litre of suspension = 1·985 grams.

Electrolyte.		Quantity in gram-mols. per cent.	Type of emulsion.	Stability.
KCl		0·005	O in W	Stable.
K₂SO₄		0·005	,,	,,
Ba(NO₄)₂	1	0·003	,,	,,
	2	0·004	,,	,,
	3	0·006	,,	,,
Al₂(SO₄)₃	1	0·001	,,	,,
	2	0·003	W in O	Stable, though some water separates on agitation.
	3	0·004	,,	
K₃PO₄	1	0·003	O in W	Stable.
	2	0·005	,,	,,
	3	0·006	,,	,,
Th(NO₃)₄	1	0·0001	,,	,,
	2	0·00035	W in O	Stable, water separating on agitation.
	3	0·0005	,,	
HCl	1	0·0003	O in W	
	2	0·0004	W in O	,,
	3	0·00045	,,	,,

Rosin.

The rosin used was the sample known as the " Seven Star Brand."
The finely powdered material was shaken for several hours with a
large quantity of water to remove any gummy substance which
might have been added to it to increase its weight. After being
filtered, the powdered rosin was dried in a current of hot air,
dissolved in absolute alcohol, and recovered by evaporation of the
solvents. The alcoholic solution was slightly acid, which is a
well-known property of many of the pure rosins.

TABLE V.

Amount of aqueous phase = 20 c.c.
Amount of oil phase = 20 c.c.
Amount of rosin = 3 grams per litre.

Electrolyte.		Quantity in gram-mols. per cent.	Type of emulsion.	Stability.
KCl	1	0·002	W in O	Quite stable.
	2	0·003	,,	,,
	3	0·006	,,	,,
K$_2$SO$_4$	1	0·003	,.	,,
	2	0·004	,,	,,
	3	0·006	,,	,,
K$_3$PO$_4$	1	0·003	,,	,,
	2	0·006	O in W	,,
	3	0·008	,,	,,
KOH	1	0·001	W in O	,,
	2	0·002	O in W	,,
	3	0·003	,,	,,

Discussion of Results.

From the results shown in Tables I—VI it is easily seen that
aluminium hydroxide, zinc hydroxide, lead oxide, and rosin, pre-
pared according to the methods described above and freed from
alkali and alkaline salts like tripotassium phosphate, yield emul-
sions of the water-in-oil type; casein, lecithin, and egg-albumin
yield emulsions of the reverse type. In the case of aluminium
hydroxide, the emulsions are unstable in the region water-in-oil.
The addition of a small quantity of potassium hydroxide, tri-
potassium phosphate, or sodium carbonate to the aqueous phase
makes emulsions of the oil-in-water type quite stable, and the
original, unstable water-in-oil type of emulsion can be reproduced
by the addition of a small amount of an acid. Just before the
point of complete inversion there is a tendency for the emulsions
to go through a zone of instability, and in most cases, especially
when the quantity of the emulsifying agent is large, this zone o

Stable oil-in-water emulsion.

Unstable emulsion.
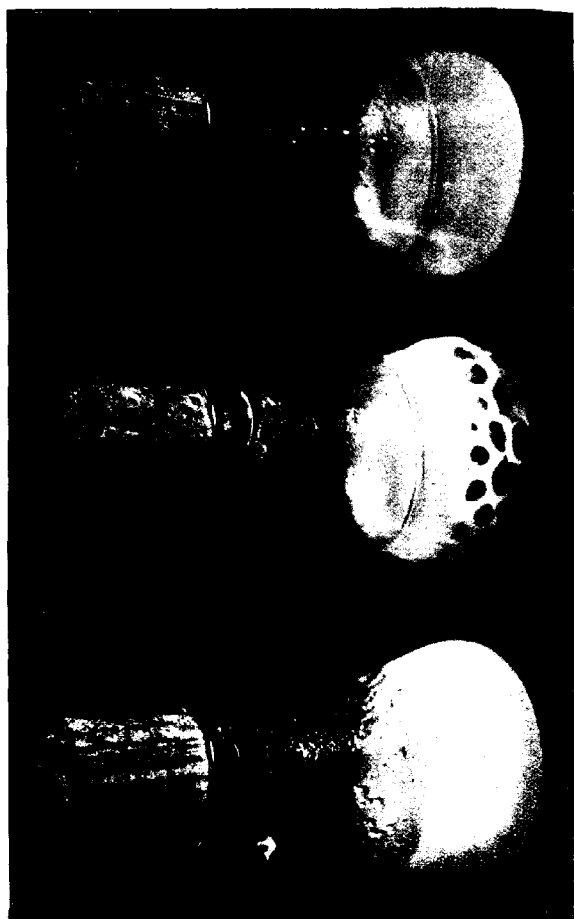
Stable water-in-oil emulsion.

instability can be seen. Plate I, which represents the oil-in-water type, the unstable zone, and the water-in-oil type, is a photograph of emulsions prepared by using lead oxide as emulsifying agent, the reversing electrolyte employed being potassium hydroxide.

It is interesting to note that all emulsions described in this paper can be made to undergo a reversal of type by suitable electrolytes, and the following empirical rules appear to hold good :

1. An emulsion of water in oil can be transformed into one of oil in water by electrolytes having reactive anions like OH′ and PO_4'''.

2. An emulsion of oil in water can be transformed into the reverse type by electrolytes having reactive cations like H˙, Al˙˙˙, Fe˙˙˙, and Th˙˙˙˙.

A somewhat similar conclusion has been drawn by Clowes (*J. Physical Chem.*, 1916, **20**, 407), who showed an intimate connexion between the effect of electrolytes on the permeability of soap films to water and the reversal of phases in emulsions. Employing a modification of Donnan's pipette, he obtained some interesting results, which showed that the protective ratios of various electrolytes on soap films are approximately logarithmic and correspond roughly with the precipitating effects exerted by the cations in question on soap dispersed in water. The fact that similar, approximately logarithmic, ratios have been observed during the study of the effects of bi- and ter-valent cations on a variety of colloidal and biological systems (Loeb and Beutner, *ibid.*, 1913, **17**, 288) lends strong support to the view that we are dealing with adsorption phenomena. In the light of these results, Clowes made the significant classification of these antagonistic electrolytes into two groups. " The first consists of di- and tri-valent cations, etc., which possess a more readily adsorbed kation and promote the formation of the emulsion of water-in-oil; the second consists of alkalis, salts of monovalent kations and of di- and tri-valent anions which possess a more reactive and more readily adsorbed anion, and appear to exert the reverse effect of promoting the formation of oil dispersed in water."

According to Bancroft, the type of emulsion obtained depends on whether the emulsifying agent is more soluble in water or in oil. The introduction of the idea of solubility in one phase or the other is an extension of the rule, first put forward by Pickering, that the main factor determining the formation of one type or the other is whether the emulsifying agent is more easily wetted by the oil or by the water. The original view of Pickering is to be preferred; first, because the physical explanation of the phenomenon as given by Bancroft introduces certain complications into

our ideas of interfacial tension, and it is by no means easy to under-
stand the two interfacial tensions of a film formed by the concen-
tration of the dissolved substance at the interface according to
the Gibbs-Thomson law, and more especially so when the film is
assumed to be freely permeable to at least one of the two phases
of the emulsions; secondly, for the reason that some bivalent soaps
like calcium oleate, barium linoleate, calcium linoleate and palmitate,
barium oleate, and zinc stearate, etc., are almost as insoluble in
kerosene oil and benzene as in water, and certain univalent soaps,
like sodium and potassium oleates, stearates, and linoleates, are
soluble in oils as well as in water.   Further, there are many sub-
stances which dissolve either in water or in oil and lower the surface
tension and yet do not form emulsions.   Donnan and Terroine,
Mayer, Schaeffer (*Compt. rend.*, 1908, **146**, 484), and lately Fischer,
Hooker, and Clayton (*J. Soc. Chem. Ind.*, 1919, **38**, 113T—118T)
have pointed out that the emulsifying agent must be colloidal in
nature, and it is probable that an explanation of the reversal of
type by electrolytes is to be found in the nature of the adsorption
by the colloidal surface films which envelop the globules.   It is
no doubt true that one may get some idea of the wetting power
of a liquid by its property of dissolving a particular substance,
but it is well known that the argument cannot be pushed too far,
and many a substance, although insoluble in certain liquids, may
yet be wetted by them.   It is also well known that soaps are
precipitated by the addition of univalent electrolytes, and in fact
this action of sodium chloride has been taken advantage of in the
technical manufacture of soap in the process of " salting out."
It is very difficult to draw a hard and fast line between the effects
of univalent electrolytes and of bi- and ter-valent electrolytes on
soap solutions, as both of these are adsorption phenomena.   On
the solubility hypothesis, sodium chloride ought to be capable of
changing the type as well as barium chloride.   This is, however,
contrary to all experience, and the multivalent ions alone are known
to cause the reversal of type.   There is thus a striking resemblance
between these effects of the electrolytes on the reversal of type and
the reversal of charge on t' e colloid emulsifier, and it lends strong
support to the view, first put forward by Clowes, that the antagon-
istic effects of electrolytes are attributable to a balance between
the cations on the one hand, and the anions on the other, adsorbed
by or reacting with the constituents of the surface film or membrane.

The classical researches of Loeb (*Biochem. Zeitsch.*, 1912, **39**,
127; 1913, **51**, 88) on the effects of reactive cationic electrolytes
on lipoids, lecithin, protein, and casein show that they react with
them so as to form water-insoluble salts oppositely charged to the

original lipoids.   In explaining the analogous behaviour of certain biological and protoplasmic systems, Mines (*J. Physiol.*, 1912, **43**, 467), Loeb and Beutner (*loc. cit.*), and Clark (*J. Physiol.*, 1913, **47**, 66) have emphasised the importance of both these effects.

The data on the question of the formation of the water-in-oil and the oil-in-water emulsions and their transformation into one form or the other are restricted (1) to results on various soaps by Newman, Clowes, Briggs, and Bhatnagar, and (2) to the work of Pickering and the results embodied in this paper.   For the sake of closer comparison, a table of the emulsifying agents so far tried and of the electrolytes which reverse the type is shown below.

TABLE VI.

Emulsifying agent.	Reversing electrolyte : Salts of	Type of emulsion.	Nature of the adsorption compounds ; + represents excess of adsorption of positive ions, — represents excess of adsorption of negative ions.
Sodium oleate	Ba, Ca, Sr, Fe, Cr, Al, Cu, Zn, Ni	O in W	+
Carbon	KOH, K₃PO₄	W in O	—
Casein	Al, Fe, Th, H	O in W	+
Albumin			+
Zinc hydroxide	KOH, K₃PO₄	W in O	—
Zinc hydroxide (alkaline)	Al, Th, H	O in W	+
Aluminium hydroxide	KOH, K₃PO₄	W in O	—
Lead oxide	KOH	,,	—
Rosin	K₃PO₄, KOH	,,	—
Lecithin	Al, Fe, Th	O in W	+
Univalent soaps	Bivalent and tervalent metals	,,	+

From a close study of the data on the reversal of type in emulsions, it is easily seen that the effects of the electrolytes on the surface film of the globules in emulsions are precisely similar to those on lipoids and protoplasm (Loeb and Osterhout, *loc. cit.*). Substances like tripotassium phosphate and potassium hydroxide have a decided effect on the wetting property of zinc, lead, and aluminium hydroxides, as well as on their surface potential, and a rational theory of emulsification should be capable of including and explaining the facts emphasised here.   Wetting power is considered to be connected with interfacial tension, and therefore the two vital factors constituting a complete theory of the reversal of phases will be : (1) the nature of the charge on the emulsifying agent, and (2) its interfacial tension relations with the two phases. Unfortunately, our knowledge of the interfacial tension between

solids and liquids is very limited, and for the present the entire data on the reversal of type are in agreement with the empirical rule " *that all emulsifying agents having an excess of negative ions adsorbed on them and wetted by water will yield oil-in-water emulsions, whilst those having an excess of adsorbed positive ions and wetted by oil will give water-in-oil emulsions.*"

It is to be noted that emulsions prepared by gelatin and saponin do not undergo the reversal of type. Cataphoresis experiments on these emulsions show that the addition of bi- and ter-valent electrolytes changes the charge on the oil particles themselves. This is directly opposite to what happens in the case of soaps and casein. In these cases, owing to a complex chemico-adsorption process, the multivalent ions are almost wholly used up by the surface film, and the original negative charge on the oil is not disturbed. The protective film, having adsorbed, say, multivalent cations, is capable of protecting only similarly charged particles, a fact well known in colloidal chemistry.   The positive particles in this case are water globules, and it is these particles which are now protected by the adsorbed surface film.

Summary.

1. The effects of various electrolytes on emulsions prepared by the use of zinc hydroxide, aluminium hydroxide, lead oxide, casein, rosin, and egg-albumin as emulsifying agents have been studied.

2. Univalent electrolytes are incapable of reversing the type of soap emulsions, even although they throw out the soap from solution.

3. An excess of adsorbed positive ions on the surface membrane leads to the formation of the water-in-oil type of emulsion. The reverse type is produced by the adsorption of negative ions.

4. All emulsions, whether prepared by soluble emulsifiers such as soaps or by insoluble ones such as zinc hydroxide, follow the empirical rule first suggested by Clowes.

5. Evidence has been accumulated which favours the view that the relative wetting powe. of the two phases with respect to the emulsifying agent and the surface potential of the membrane between them are the two main factors governing the process of emulsification, and that the reversal of phases in emulsions by electrolytes is brought about by the changes produced in the surface membrane with regard to either or both of these two factors.

Donnan, F.R.S., for his helpful criticism and suggestions. His thanks are also due to Mr. H. I. Higson for taking some photographs of the emulsions and to his friends, Dr. J. C. Ghosh and Mr. J. N. Mukherjee.

CC.—*Crystallographic Descriptions of some Pyridine and Picoline Derivatives.*

By MARY WINEARLS PORTER.

THE following crystallographic descriptions are an extension of work published in a former paper with T. V. Barker (T., 1920, 117, 1303) dealing with a study of the morphological and structural effects produced by the mutual replacement of simple organic radicles. The results of the present investigation are summarised in the following table :

No.	Substance.	$a : b : c.$	$\beta.$	Cleavage.
1	$3C_5H_5NMeI,4HgI_2$	$0\cdot5106 : 1 : 0\cdot2182$	—	$\{100\}$ and $\{110\}$
2	$3C_5H_5NEtI,4HgI_2$	$0\cdot6473 : 1 : 0\cdot7728$	—	$\{001\}$
3	C_5H_5NPrI,HgI_2	$1\cdot9897 : 1 : 0\cdot6860$	$95°\ 41'$	$\{001\}$
4	$C_5H_4MeNMeI,HgI_2$	$0\cdot8416 : 1 : 1\cdot3697$	$99°\ 15'$	$\{010\}$
5	$C_5H_4MeNEtI,HgI_2$	$1\cdot2784 : 1 : 0\cdot5700$	$93°\ 6'$	$\{110\}$
6	$C_5H_4MeNPrI,HgI_2$	$1\cdot1654 : 1 : 0\cdot7310$	$98°\ 32'$	$\{\bar{1}01\}, \{120\}, \{021\}$

In view of the different type of chemical composition, no crystallographic similarity is to be expected between the first pair of compounds on the one hand and the remaining four on the other. But isomorphism might well be expected within either of the subgroups concerned—especially, perhaps, in the case of the isomeric compounds numbered 3 and 5 in the table. A careful study, however, fails to reveal any close similarity in angles; neither is there any similarity in the cleavage directions. The results, accordingly, afford a strong support to the conclusion drawn in the previous paper, that crystalline form is a highly sensitive, constitutive property, an increment of composition equal to CH_2, or even a slight shift of a simple radicle, being sufficient to cause the molecules to adopt a different type of arrangement when the substance assumes the crystalline state of aggregation.

EXPERIMENTAL.

The methods of preparation and analysis of the various compounds have been fully described previously (*loc. cit.*). The following are the detailed results.

Methylpyridinium Mercuri-iodide, $3C_5H_5NMeI,4HgI_2$.—M. p. 125° (Found : Hg = 32·13. Calc., Hg = 32·27 per cent.). Orthorhombic, $a : b : c = 0·5106 : 1 : 0·2182$. Forms : $b\{010\}$, $a\{100\}$, $m\{110\}$, $r\{101\}$, $t\{121\}$, $s\{141\}$. The habit is prismatic, as shown in Fig. 1. Six crystals were measured and the results are given
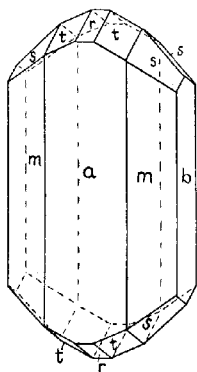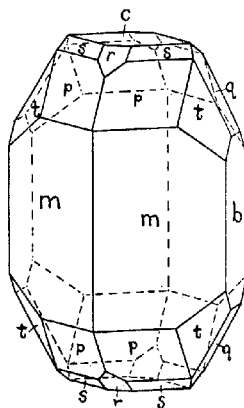
FIG. 1.   FIG. 2.

No. 1. *Methylpyridinium*   No. 2. *Ethylpyridinium*
      mercuri-iodide.   *mercuri-iodide.*

below, the deviations of the computed from the measured angular values being added in parentheses.

	$b\{010\}$.	$a\{100\}$.	$m\{110\}$.
φ	0° 7′ (−7′)	90° 17′ (−17′)	*62° 57′
ρ	90 0 (0′)	90 1 (−1′)	90 0 (0′)

	$r\{101\}$.	$t\{121\}$.	$s\{141\}$.
φ	89° 52′ (+8′)	44° 20′ (+4′)	26° 2′ (+3′)
ρ	23 9 (0′)	*31 25	44 14 (−3′)

Cleavages : $a\{100\}$, good; $m\{110\}$, imperfect. Optic axial plane, $c(001)$; acute negative bisectrix perpendicular to $b(010)$; wide axial angle; birefringence and dispersion strong.

Ethylpyridinium Mercuri-iodide, $3C_5H_5NEtI,4HgI_2$.—M. p. 79° (Found : Hg = 31·44. Calc., Hg = 31·73 per cent.). Ortho-

rhombic, $a : b : c = 0.6473 : 1 : 0.7728$. Forms: $b\{010\}$, $m\{110\}$, $c\{001\}$, $q\{021\}$, $r\{102\}$, $p\{111\}$, $s\{112\}$, $t\{121\}$. The habit is prismatic, as shown in Fig. 2. Four crystals were measured with the following results.

	$b\{010\}$.	$m\{110\}$.	$c\{001\}$.	$q\{021\}$.
ϕ	$0° 0' (0')$	$*57° 5'$	—	$0° 1' (-1')$
ρ	$90\ 0\ (0')$	$90\ 0\ (0')$	$0° 0' (0')$	$*57\ 6$

	$r\{102\}$.	$p\{111\}$.	$s\{112\}$.	$t\{121\}$.
ϕ	$89° 59' (+1')$	$57° 3' (+2')$	$57° 3' (+2')$	$37° 38' (+2')$
ρ	$30\ 45\ (+6')$	$54\ 55\ (0')$	$35\ 23\ (+3')$	$62\ 50\ (+3')$

Cleavage : $c\{001\}$, perfect.

FIG. 3.   FIG. 4.

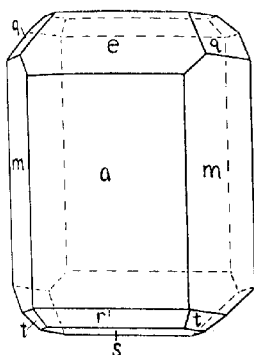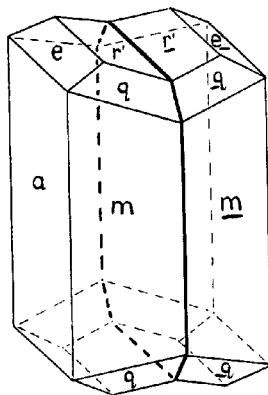No. 3. *Propylpyridinium*   No. 3.   *Propylpyridinium*
mercuri-iodide (simple crystal).   *mercuri-iodide (twin crystal).*

Propylpyridinium Mercuri-iodide, C_5H_5NPrI,HgI_2.—M. p. 95° (Found : Hg = 28.41. Calc., Hg = 28.45 per cent.). Monoclinic, $a : b : c = 1.9897 : 1 : 0.6860$; $\beta = 95° 41'$. Forms : $a\{100\}$, $m\{110\}$, $q\{011\}$, $e\{101\}$, $r'\{\bar{1}01\}$, $s\{\bar{3}01\}$, $t\{\bar{2}11\}$. The habit, as shown in Fig. 3, is tabular parallel to $a\{100\}$ and elongated along the c-axis. Crystals twinned on $a(100)$ are frequent (see Fig. 4). Four crystals were measured with the following results.

	$a\{100\}$.	$m\{110\}$.	$q\{011\}$.	$e\{101\}$.
ϕ	$90° 2' (-2')$	$*26° 48'$	$*8° 15'$	$90° 9' (-9')$
ρ	$90\ 0\ (0')$	$90\ 0\ (0')$	$*34\ 44$	$23\ 58\ (+3')$

	$r'\{\bar{1}01\}$.	$s\{\bar{3}01\}$.	$t\{\bar{2}11\}$.
ϕ	$270° 7' (-7')$	$270° 0' (0')$	$319° 11' (0')$
ρ	$13\ 53\ (-2')$	$43\ 18\ (-7')$	$42\ 18\ (-6')$

3 P *

Cleavage : $c\{001\}$, fairly good. The optic axial plane is perpendicular to the symmetry plane. The negative acute bisectrix emerges through $c(001)$. The double refraction is strong, and the axial angle is wide. Dispersion $\rho < v$.

Methyl-α-picolinium Mercuri-iodide, $C_5H_4MeNMeI,HgI_2$.—M. p. 134° (Found : Hg = 29·03. Calc., Hg = 29·03 per cent.). Monoclinic, $a : b : c = 0·8416 : 1 : 1·3697$; $\beta = 99° 15'$. Forms : $a\{100\}$, $m\{100\}$, $c\{001\}$, $q\{011\}$, $e\{201\}$, $p\{111\}$, $s\{\bar{2}11\}$. The habit is prismatic,
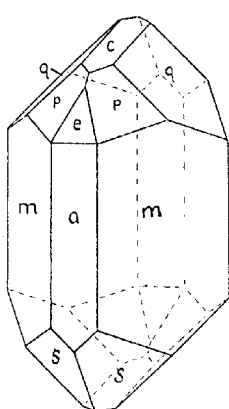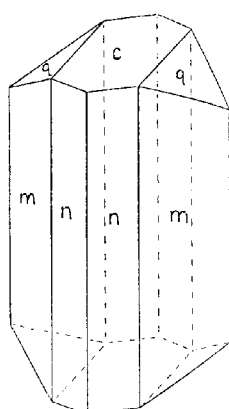
Fig. 5. | Fig. 6.

No. 4. *Methyl-α-picolinium mercuri-iodide.*

No. 5. *Ethyl-α-picolinium mercuri-iodide.*

as shown in Fig. 5. Three crystals were measured, and the results are given in the table below.

	$a\{100\}$.	$m\{110\}$.	$c\{001\}$.	$q\{011\}$.
ϕ	90° 0′ (0′)	*36° 29′	89° 55′ (+5′)	10° 54′ (+3′)
ρ	90 0 (0′)	90 0 (0′)	9 10 (+5′)	40 33 (+3′)

	$e\{201\}$.	$p\{111\}$.	$s\{\bar{2}11\}$.
ϕ	90° 1′ (−1)	*43° 1′	307° 53′ (−1′)
ρ	54 40 (−3′)	*49 1	53 56 (−2′)

Cleavage : $b\{010\}$, imperfect. Optic axial plane $b(010)$; the positive acute bisectrix is visible through a section perpendicular to the prism zone. The second mean line α emerges nearly perpendicular to $a(100)$. The axial angle is wide.

Ethyl-α-picolinium Mercuri-iodide, $C_5H_4MeNEtI,HgI_2$.—M. p. 99° (Found : Hg = 28·50. Calc., Hg = 28·45 per cent.). Monoclinic,

$a : b : c = 1\cdot2784 : 1 : 0\cdot5700$; $\beta = 93°\,6'$. Forms : $a\{100\}$, $m\{110\}$, $n\{210\}$, $c\{001\}$, $q\{011\}$, $s\{201\}$. The habit is shown in Fig. 6 and is slender prismatic. Five crystals were measured, and the results are given below.

	$a\{100\}$.	$m\{110\}$.	$n\{210\}$.
ϕ	89° 56′ (+4′)	*38° 4′	57° 6′ (+21′)
ρ	90 0 (0′)	90 0 (0′)	90 0 (0′)

	$c\{001\}$.	$q\{011\}$.	$s\{201\}$.
ϕ	90° 17′ (−17′)	*5° 26′	90° 13′ (−13′)
ρ	3 6 (0′)	*29 48	43 58 (−31′)

Cleavage : $m\{110\}$, imperfect. Optic axial plane $b(010)$. An optic axis is visible through $a(100)$ with strong dispersion.

Propyl-α-picolinium Mercuri-iodide, $C_5H_4MeNPrI,HgI_2$.—M. p. 85° (Found : Hg = 27·93. Calc., Hg = 27·89 per cent.). Monoclinic, $a : b : c = 1\cdot1654 : 1 : 0\cdot7310$; $\beta = 98°\,32'$. Forms : $a\{100\}$, $n\{120\}$, $s\{021\}$, $e\{101\}$, $r\{\bar{1}01\}$, $t\{221\}$, $w\{341\}$. The habit, as shown in Fig. 7, is tabular parallel to $a(100)$ and elongated along the b-axis. Four crystals were measured and the results are given in the table below.

	$a\{100\}$.	$n\{120\}$.	$s\{021\}$.
ϕ	89° 58′ (+2′)	*23° 37′	*5° 51′
ρ	90 0 (0′)	90 0 (0′)	*55 46

	$e\{101\}$.	$r\{\bar{1}01\}$.
ϕ	89° 57′ (+3′)	269° 50′ (+10′)
ρ	38 11 (−5′)	25 56 (−6′)

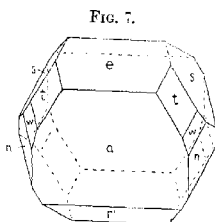|	$t\{221\}$.	$w\{341\}$.
ϕ	44° 8′ (+1′)	35° 17′ (−14′)
ρ	63 47 (+4′)	74 20 (+2′)

Fig. 7.

No. 6.   *Propyl-α-picolinium mercuri-iodide.*

Cleavages : $r\{\bar{1}01\}$ and $n\{120\}$, perfect; $s\{021\}$, imperfect. The optic axial plane is perpendicular to the plane of symmetry and the symmetry axis b- is the acute positive bisectrix. Through $n(120)$ an optic axis is visible. The dispersion is strong $\rho < v$.

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CCI.—*Studies of Halogenohydrins and Related Derivatives in the Cinnamic Acid Series. Part I.*

By JOHN READ and ALBERTA CATHERINE PRITCHARD ANDREWS.

DESPITE the importance of the halogenohydrins of cinnamic acid, the methods hitherto adopted for their preparation are probably little more efficient than those which have been used in making ethylenebromohydrin and other similar derivatives (Read and Hook, T., 1920, **117**, 1214). It is obvious, for example, that the preparation of the bromohydrin of cinnamic acid (α-bromo-β-hydroxy-β-phenylpropionic acid) by boiling the dibromide with water (Glaser, *Annalen*, 1868, **147**, 84; Erlenmeyer, *Ber.*, 1880, **13**, 310) cannot be commended; and although the corresponding chlorohydrin has been made by utilising the principle of direct addition of hypochlorous acid, the yields were unsatisfactory, owing to the conditions adopted. Thus, Glaser (*loc. cit.*, p. 80), in order to avoid the long and troublesome preparation of dilute solutions of hypochlorous acid, passed chlorine into a cold mixture of equivalent proportions of sodium cinnamate and sodium carbonate, thereby obtaining a yield of 35 per cent. of chlorohydrin; and Erlenmeyer and Lipp (*Annalen*, 1883, **219**, 185) described a modified method which was stated to give about 64 per cent. of the calculated amount of chlorohydrin, after allowing for the considerable proportion (22 per cent.) of unchanged cinnamic acid. In contrast to these methods, it has recently been shown that by the action of cold dilute bromine water on an aqueous suspension of cinnamic acid a yield of more than 80 per cent. of bromohydrin is readily obtained (Read and Williams, *J. Proc. Roy. Soc. N.S. Wales*, 1917, **51**, 558).

It may now be pointed out that since, in the last-named method, the yield of bromohydrin fell to about 50 per cent. when sodium cinnamate was substituted for cinnamic acid, some doubt was thrown upon the advisability of using sodium or potassium cinnamate in the preparation of the corresponding chlorohydrin, according to the methods recommended by the above-mentioned investigators. An examination of the second of these methods, which, judging from its repeated application (compare *Ber.*, 1906, **39**, 788), seems to have been the best hitherto available for the preparation of cinnamic acid chlorohydrin (α-chloro-β-hydroxy-β-phenylpropionic acid), has convinced us that the yield recorded by Erlenmeyer and Lipp is rarely, if ever, attained. Further, there is no justification for Glaser's statement (*loc. cit.*) that hypochlorous acid combines

with free cinnamic acid only with difficulty, whilst combination with alkali cinnamates takes place more easily. We have, in fact, been able to devise a simple and expeditious method of effecting almost quantitatively the direct addition of hypochlorous acid to cinnamic acid, by the use of cold chlorine water; it has also been found possible to improve the yield of bromohydrin correspondingly. The reactions concerned may be represented in terms of a mobile equilibrium, in accordance with the scheme already suggested in the similar case of ethylene :

$$X_2 \quad + \quad HOH \rightleftharpoons HX + HOX$$

$$Ph \cdot CHX \cdot CHX \cdot CO_2H \qquad\qquad Ph \cdot CH(OH) \cdot CHX \cdot CO_2H.$$
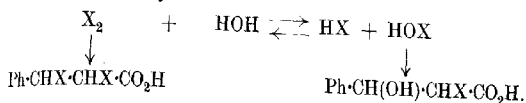
With cinnamic acid and bromine water, the displacement to the right is even more pronounced than with ethylene under similar conditions : at a concentration of $0 \cdot 08.N$ no less than 98 per cent. of the cinnamic acid was transformed to bromohydrin, the corresponding value for ethylene being 94 per cent. In view of the ease with which cinnamic acid reacts with chlorine water or bromine water to produce halogenohydrins, endeavours were made to utilise iodine in a similar way; but up to the present it has not been possible to prepare iodohydrins by this method. Attempts to effect additive reactions with cyanic acid have also failed.

Hitherto, little attention seems to have been directed towards the halogenohydrins of substituted cinnamic acids : in the present paper, some preliminary investigations in this field, dealing with the o-methoxycinnamic acids, are described. Like cinnamic acid, these two stereoisomeric derivatives react with bromine water to give almost quantitative yields of bromohydrin, the same crystalline derivative being produced from each. Owing to the simultaneous entry of a bromine atom into the benzene nucleus, it was not possible to prepare the interesting o-methoxyphenylacetaldehyde, but the method of Erlenmeyer and Lipp (loc. cit., p. 182), when applied to this new bromohydrin, led easily to 5-bromo-2-methoxyphenylacetaldehyde : it is evident, as a further outcome of this work, that cinnamic acid may similarly be transformed with great facility into phenylacetaldehyde, by the successive action of chlorine water, sodium hydroxide solution, and dilute sulphuric acid.

Although additive reactions of cinnamic acid with chlorine and bromine lead readily to the formation of the two externally compensated, stereoisomeric dichlorides and dibromides demanded by theory (Ber., 1894, 27, 2039; 1895, 28, 2235), yet in the similar reactions with hypochlorous and hypobromous acids only one such substance was isolated in each case. Notwithstanding the adoption

of conditions which would seem to favour the production of the more labile stereoisomeride, no definite indications of the presence of a more soluble derivative were observed; but it may be mentioned that small quantities of oily material were deposited by the mother-liquors from the recrystallisation of comparatively large amounts of the solid derivatives (compare Erlenmeyer and Moebes, *Ber.*, 1899, **32**, 2377). On the other hand, the crystalline bromohydrin from methylcoumarinic and methylcoumaric acids was associated with pronounced quantities of a viscous oil, which appeared to consist of a slightly impure isomeric derivative and was pro-duced to about the same extent in each case. Like the related dihalogenides and halogenohydrins of cinnamic acid, the new crystalline bromohydrin has been resolved into optically active components, the small molecular rotatory powers of which suggest stereochemical analogy with cinnamic acid derivatives rather than with those of *allo*cinnamic acid (compare Liebermann, *Ber.*, 1894, **27**, 2041). It is interesting to note that although methylcoumarinic acid reacts with chlorine or bromine much more rapidly than does methylcoumaric acid, yet the two acids exhibit no appreciable difference in the ease of their reaction with bromine water. Further, the influence of sunlight, which is marked in the addition of halogens, is negligible in the formation of halogenohydrins from these acids and cinnamic acid.

EXPERIMENTAL.

The Addition of Hypochlorous Acid to Cinnamic Acid.

On passing a slow stream of chlorine, with vigorous stirring, into a suspension of finely crystalline cinnamic acid in about thirty times its weight of ice-cooled water, in accordance with the method used with success in the case of bromine (Read and Williams, *loc. cit.*), a very low yield of chlorohydrin was obtained, and about 60 per cent. of the cinnamic acid was recovered unchanged. This result, which was the same when freshly precipitated cinnamic acid was used, must probably be ascribed to the envelopment of particles of cinnamic acid by the semi-solid aggregations of cinnamic acid dichloride and chlorostyrene which are produced under these conditions. The difficulty was eventually overcome in the following manner :

Cinnamic acid (20 grams) was dissolved in 2*N*-sodium hydroxide solution (67 c.c.) with the aid of an appropriate addition of water (200 c.c.). The resulting solution of sodium cinnamate was then added drop by drop to a large volume (1600 c.c.) of ice-cooled water, acidified with a little (2 c.c.) concentrated sulphuric acid, and a

slow stream of chlorine, prepared from hydrochloric acid and bleaching powder, was passed simultaneously into the liquid through a small perforated bulb, admixture being effected by means of vigorous mechanical stirring. Conditions were so adjusted as to maintain a faint yellow tinge in the liquid, and the cinnamic acid liberated from each few drops of sodium cinnamate solution was allowed to react completely before the admission of a further quantity. Reaction occurred rapidly, and when all the cinnamic acid had been introduced the liquid was stirred for some time with passage of air, in order to expel excess of chlorine : the reaction mixture then consisted of a clear colourless liquid, surmounting a small quantity of white solid matter. Preliminary experiments with aqueous solutions of the pure chloro- and bromo-hydrin of cinnamic acid indicated that the amount of chlorine (or bromine) which had reacted to form halogenohydrin and hydrogen chloride (or bromide) could be determined by titrating a small aliquot portion of the liquid with standard silver nitrate solution, using Volhard's method (Read and Hook, *loc. cit.*), a slight correction being applied in accordance with the results of a control experiment in which chlorine was passed into water under similar conditions. Data obtained in this way indicated that more than 95 per cent. of the cinnamic acid had reacted to form chlorohydrin; the corresponding value found for ethylene at the same molecular concentration ($0.07N$) was 94 per cent. (*loc. cit.*).

The solid product of the reaction (0·4 gram) consisted of cinnamic acid dichloride, and by extracting the aqueous liquid with light petroleum a small quantity (1·5 grams) of chlorostyrene was isolated. The proportion of cinnamic acid involved in the formation of these by-products is about 9 per cent.; consequently, the yield of chlorohydrin, calculated by difference, is 91 per cent. This result stands in good agreement with the value determined by titration. The ethereal extract of the acid liquid, when dried over sodium sulphate and distilled from the water-bath, yielded a crystalline residue (23·8 grams), which was identified as the anticipated cinnamic acid chlorohydrin, $OH \cdot CHPh \cdot CHCl \cdot CO_2H, H_2O$, m. p. 78—80° (Found: $Cl = 16\cdot1$. $C_9H_9O_3Cl, H_2O$ requires $Cl = 16\cdot25$ per cent.). The pure substance crystallises well from hot water, as also from hot benzene or toluene; it separates readily from moderately strong aqueous solutions, in the form of a crystalline precipitate, on the addition of dilute sulphuric acid.

The amount of solid chlorohydrin (23·8 grams) actually isolated in the above experiment, when the acid liquid was extracted three times with ether, corresponded with a yield of 80·1 per cent., calculated from the weight of cinnamic acid used. It is essential

that the halogen should react with cinnamic acid in presence of the rather large volume of water indicated above: in an experiment conducted with half this volume of water, the other conditions remaining unaltered, about half the cinnamic acid was unaffected, and appreciable quantities of cinnamic acid dichloride and chloro-styrene were produced. It is also advisable to dilute the chlorine with air, in order to minimise the formation of these by-products.

The Addition of Hypobromous Acid to Cinnamic Acid.

The results of the above investigation suggested that the yield of bromohydrin might likewise be increased by precipitating the cinnamic acid, little by little, in the reaction vessel, during the passage through the liquid of a slow stream of air charged with bromine vapour. Upon treating 20 grams of cinnamic acid in this way, reaction occurred with great ease, and a titrimetric deter-mination of the resulting hydrogen bromide indicated that 98 per cent. of the cinnamic acid had reacted to form bromohydrin; the value calculated by difference, taking into account the small amounts of cinnamic acid dibromide and bromostyrene produced, was only slightly lower than this; and the weight (30·3 grams) of solid bromohydrin, $OH \cdot CHPh \cdot CHBr \cdot CO_2H, H_2O$, isolated by extracting the acid liquid three times with ether, corresponded with a yield of 85·4 per cent. After one recrystallisation from hot toluene, the product melted at 120—122° and was anhydrous (Found: Br = 32·5. $C_9H_9O_3Br$ requires Br = 32·7 per cent.). By the original method, using finely crystalline cinnamic acid suspended in only three-eighths the above volume of water, the yield of bromo-hydrin actually isolated was 76·3 per cent. It seems, therefore, that dilution of the solution and dispersion of the cinnamic acid is more important when working with chlorine than with bromine.

In examining various other aspects of this method, it was found that the introduction of the bromine in the form of liquid, rather than as vapour, depressed the yield of bromohydrin from 98 to 82 per cent., a larger amount of cinnamic acid dibromide being formed in this case. At the ordinary temperature, the absorption of bromine was slower than in the cold; more dibromide was formed, and the yield of bromohydrin fell to 89 per cent. Sunlight appeared to have no marked effect on the reaction.

Some Salts of α-Bromo-β-hydroxy-β-phenylpropionic Acid.

During the course of the above work it was noticed that cinnamic

acid bromohydrin forms characteristic, well-defined salts, and some of these are now described. The *zinc* salt,

$$(OH \cdot CHPh \cdot CHBr \cdot CO_2)_2Zn, 5H_2O,$$

crystallises in lustrous needles when the solution obtained by dissolving zinc carbonate in a warm aqueous solution of the acid is allowed to cool [Found: Br = 24·8. $(C_9H_8O_3Br)_2Zn, 5H_2O$ requires Br = 24·8 per cent.]. The *copper* salt,

$$(OH \cdot CHPh \cdot CHBr \cdot CO_2)_2Cu, 5H_2O,$$
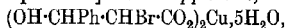
prepared in a similar manner, forms pale blue needles [Found: Cu = 9·7. $(C_9H_8O_3Br)_2Cu, 5H_2O$ requires Cu = 9·9 per cent.].

Special interest attaches to the *brucine* salt,

$$OH \cdot CHPh \cdot CHBr \cdot CO_2H, C_{23}H_{26}O_4N_2,$$
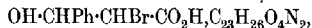
which is highly characteristic of the acid. When equivalent amounts of the acid and brucine were mixed in alcoholic solution, no separation of crystalline material occurred, and evaporation on the water-bath left a vitreous residue. After keeping for a few days, the mass became crystalline when rubbed with methyl alcohol, and by inoculating similar methyl-alcoholic solutions of the mixed acid and base with material obtained in this way the crystalline salt was prepared without difficulty in almost quantitative yield. It was sparingly soluble in water, alcohol, and most of the usual organic solvents, with the exception of chloroform; the solvent best adapted for its recrystallisation and polarimetric examination was 50 per cent. aqueous alcohol. In determining the specific rotatory power of the original separation, a weighed amount was made up to 30·0 c.c. with the solvent at 20° and examined in a 2-dcm. tube : * 0·1867 gram gave $\alpha_D - 0·19°$, whence $[\alpha]_D - 15·2°$. In the course of several recrystallisations from 50 per cent. aqueous alcohol fluctuations in rotatory power were observed, amounting to a few units on either side of the value recorded above. Small quantities of bromostyrene were produced during the concentration of the solutions. Similar results were observed when brucine was mixed with two molecular proportions of the acid (34 grams) in alcoholic solution : specimens of acid regenerated from various fractions of the salt exhibited only feeble optical activity, the highest value observed being $[\alpha]_D - 4·4°$ in 1 per cent. absolute alcoholic solution. From these data it is evident that the two salts, *d*A*l*B and *l*A*l*B, produced under the conditions described, give rise to solid solutions, in conformity with the third type of behaviour in such cases distinguished by Pope and Read (T., 1910, **97**, 989). Since well-developed crystals were easily secured, it appeared desirable to record some crystallographic data in this interesting

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* These conditions were observed in all the polarimetric determinations recorded in this paper.

example.   We are indebted to Miss Marie Bentivoglio, B.Sc., of the Geology Department, University of Sydney, for the appended description and goniometric measurements, which were made on crystals selected from a fraction having $[\alpha]_D - 13\cdot2°$ (Found : N $= 4\cdot4$. $C_{32}H_{35}O_7N_2Br$ requires N $= 4\cdot4$ per cent.).
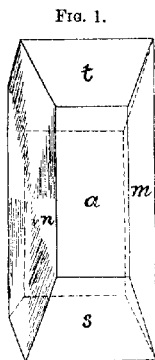
FIG. 1.

Eight crystals were selected for goniometric work; these were small, rather well-developed, and similar in appearance The crystals are colourless and transparent, and possess highly lustrous faces. The prisms are the dominant form developed; one of these assumes large proportions and is striated to give the general appearance of a star. The pinacoid $a(100)$ gives the best reflections obtained from the crystals, and these yielded only fairly satisfactory results. The basal pinacoid and clinopinacoid are entirely absent. Two domes, $s(\bar{1}01)$ and $t(101)$, are also represented. No cleavage was observed.

Crystal System : Monoclinic, hemimorphic.

Axial ratios : $a : b : c = 0\cdot9095 : 1 : 0\cdot9185$. $\beta = 93°\ 40'$.

The forms developed are : $a(100)$, $m(250)$, $n(130)$, $t(101)$, and $s(\bar{1}01)$.

The table of measurements is given below.

	Angle.		No. of measurements.	Limits.		Observed.	Calculated.
am	$= 100 : 250$	....	16	$66°\ 46'$	$—67°\ 40'$	$67°\ 06'$	$67°\ 06'$
$m\bar{m}$	$= 250 : 2\bar{5}0$	....	8	$45\ 22$	$—45\ 58$	$45\ 48$	$45\ 48$
an	$= 100 : 130$	....	16	$69\ 39$	$—70\ 23$	$69\ 50$	$69\ 50$
$n\bar{n}$	$= 130 : \bar{1}30$	....	8	$40\ 25$	$41\ 00$	$40\ 40$	$40\ 20$
at	$= 100 : 101$	....	10	$42\ 35$	$—43\ 10$	$42\ 54$	$42\ 54$
$t\bar{s}$	$= 101 : \bar{1}01$	....	11	$90\ 24$	$—90\ 42$	$90\ 32$	$90\ 32$
$\bar{s}\bar{a}$	$= 101 : \bar{1}00$	....	11	$46\ 20$	$—46\ 44$	$46\ 34$	$46\ 34$

Observations on the Optical Resolution of dl-α-Bromo-β-hydroxy-β-phenylpropionic *Acid by means of Cinchonine.*

The description given by Erlenmeyer and Moebes (*Ber.*, 1899, **32**, 2375) of the original resolution of this acid with cinchonine indicates that a single recrystallisation of the first separation of salt (37 per cent.) led to an acid having $[\alpha]_D + 21\cdot46°$ in 3 per cent. absolute alcoholic solution, and melting at 119—120°. The value $[\alpha]_D + 22\cdot6°$ has also been recorded (*Ber.*, 1906, **39**, 790); and this appreciable discrepancy, taken in conjunction with the above-

mentioned behaviour of the brucine salt, suggested a further examination of the cinchonine salt. On repeating the resolution according to the original method, but using six times the quantity of cinchonine salt (132 grams), the first separation, after one re-crystallisation from alcohol, yielded a fraction (37·75 grams) having $[\alpha]_D + 12\cdot4°$ in 0·75 per cent. alcoholic solution. A second re-crystallisation gave material (25·85 grams) having $[\alpha]_D + 11\cdot8°$, and the lustrous needles resulting from a third recrystallisation (17·6 grams) had $[\alpha]_D + 12\cdot9°$. The acid regenerated from the last-named salt was semi-solid, and after one crystallisation from benzene it gave $[\alpha]_D + 19\cdot7°$ in 3 per cent. alcoholic solution. The corresponding values after two successive recrystallisations from benzene were $+ 19\cdot6°$ and $+ 20\cdot0°$ respectively, and the melting point remained unaltered at 119° (Found : Br = 32·8. $C_9H_9O_3Br$ requires Br = 32·7 per cent.).

The acid regenerated from the mother-liquor of the first separation of cinchonine salt was also somewhat oily, but crystallisation from benzene yielded colourless needles melting at 113·114° and having $[\alpha]_D - 15\cdot1°$. Three successive recrystallisations from benzene failed to alter either the melting point or the specific rotatory power of this acid. These results appear to indicate that the two cinchonine salts, dA/B and lA/B, have some tendency to form solid solutions, and that it is not possible to purify the partly compensated acids by fractional crystallisation.

The Attempted Addition of Hypoiodous Acid and of Cyanic Acid to Cinnamic Acid.

When cinnamic acid was introduced into an aqueous solution of iodine the colour persisted, and no reaction occurred. A similar result was observed when aqueous solutions of sodium cinnamate and iodine in potassium iodide were admitted separately into a large volume of cold water acidified with sulphuric acid. The process was also varied, without success, by dissolving cinnamic acid and iodine in aqueous sodium hydroxide and adding the mixed solutions to acidified water.

Similarly, mixed aqueous solutions of sodium cinnamate and potassium cyanate were introduced slowly, with stirring, into ice-cooled water acidified with acetic acid, but the formation of an additive product could not be established. Modifications of this process were also tried without success.

These results indicate (1) that iodine water cannot be regarded as a practical source of potential hypoiodous acid, and (2) that cyanic acid has no constitutional similarity with hypochlorous acid or hypobromous acid.

The Addition of Hypobromous Acid to Methylcoumarinic Acid.

Methylcoumarinic acid, when treated with dilute bromine water in the manner outlined above for cinnamic acid, reacted very readily, but it was not possible to isolate any homogeneous product after the passage of one molecular proportion of bromine. Extraction with ether at this stage yielded a viscous oil, from which crystalline material melting indefinitely between 124° and 134° was obtained with difficulty. This gave 10·8 per cent. of bromine by alkaline hydrolysis, whereas the calculated percentage for methylcoumarinic acid bromohydrin is 29·1. The results of combustion analysis (C = 53·0; H = 4·6 per cent.) indicated that the product contained unchanged methylcoumarinic acid. Moreover, since 45 per cent. of the bromine used was eliminated as hydrogen bromide, it is evident that nuclear substitution accompanies side-chain addition in this reaction. This interesting conclusion was borne out by the results of further experiments, in which bromine was introduced in the usual manner until the attainment of a permanent faint yellow tinge : a solution of methylcoumarinic acid (20 grams) in 10 per cent. sodium hydroxide (45 c.c.), with the addition of a suitable volume of water (100 c.c.), being added slowly to a large volume (1200 c.c.) of ice-cooled water acidified with sulphuric acid (2 c.c.). The amount of bromine absorbed was slightly more than two molecular proportions; of this, 48 per cent. was eliminated as hydrogen bromide, corresponding with a 96 per cent. yield of a bromohydrin of the type

$$OMe \cdot C_6H_3Br \cdot CH(OH) \cdot CHBr \cdot CO_2H.$$
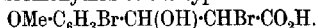
It is of interest that the yield of ethylenebromohydrin at a similar concentration (0·08N) was 93·4 per cent.

Extraction of the above acid liquid with ether gave almost the calculated amount of a viscous, brown oil; this became semi-solid on keeping, and by adding a little light petroleum, followed by sufficient benzene to clear the resulting turbid liquid, it was found possible to collect the crystalline portion by filtration. The yield (33 grams) was 82·9 per cent. of the amount theoretically possible, and the product melted at 145—150°. After two recrystallisations from hot benzene containing a little alcohol, fine, colourless leaflets were obtained, melting at 153—154° and corresponding with the formula given above (Found : C = 33·7; H = 2·9; Br, by alkaline hydrolysis = 22·5. $C_{10}H_{10}O_4Br_2$ requires C = 33·9; H = 2·8; Br/2 = 22·6 per cent.). When dissolved in warm water and oxidised at the water-bath temperature with alkaline potassium permanganate solution, it yielded an acid which, after a preliminary crystallisation from a mixture of ether and light petroleum, separated

from a hot aqueous solution in long, slender needles melting at 119°. The properties of this acid corresponded with those of 5-bromo-2-methoxybenzoic acid, described by Peratoner (*Gazzetta*, 1886, **16**, 409) (Found : C = 41·4; H = 3·2. Calc., C = 41·5; H = 3·0 per cent.). Assuming the usual mode of addition of hypobromous acid, the crystalline bromohydrin obtained from methylcoumarinic acid by the above reaction was thus α : 5-*dibromo*-β-*hydroxy*-2-*methoxy*-β-*phenylpropionic acid*. It dissolves readily in alcohol or acetone, but only sparingly in chloroform, benzene, or toluene, whilst it is almost insoluble in light petroleum. It is most conveniently crystallised from boiling benzene, with the addition of a little alcohol. When pure, it also crystallises well from hot water, in which it is moderately soluble.

The oily material obtained in the reaction contained a small quantity of the corresponding styrene derivative, but the results of alkaline hydrolysis indicated that it consisted mainly of an isomeride of the above acid (Found : Br = 21·1. $C_{10}H_{10}O_4Br_2$ requires Br/2 = 22·6 per cent.). After keeping for six months, only slight signs of crystallisation were evident, and as yet the substance has not been more fully characterised.

The Addition of Hypobromous Acid to Methylcoumaric Acid.

On introducing methylcoumaric acid into cold bromine water, in the manner already described for methylcoumarinic acid, two molecular proportions of bromine were absorbed before the appearance of a permanent yellow tinge; of this amount, 48·5 per cent. was eliminated as hydrogen bromide, indicating a yield of 97 per cent. of a bromohydrin of the type $OMe\cdot C_6H_3Br\cdot CH(OH)\cdot CHBr\cdot CO_2H$. From the ethereal extract almost the same amounts of crystalline and oily products were obtained as in the case of methylcoumarinic acid. After several recrystallisations from hot benzene containing a little alcohol, the solid derivative melted at 153—154°, and further examination of its properties showed it to be identical with the solid bromohydrin obtained from methylcoumarinic acid (Found : C = 33·7; H = 2·9; Br, by alkaline hydrolysis = 22·4. Calc., C = 33·9; H = 2·8; Br/2 = 22·6 per cent.). The oily product was also similar in appearance and properties to that yielded by methylcoumarinic acid (Found : Br, by alkaline hydrolysis = 19·7 per cent.).

Methylcoumaric and methylcoumarinic acids appeared to react with bromine water with equal ease, and in both cases parallel experiments conducted in diffused daylight and in bright sunlight led to the same results.

The Resolution of dl-α : 5-*Dibromo-β-hydroxy-2-methoxy-β-phenyl-propionic Acid into Optically Active Components.*

The *brucine* salt, $OMe \cdot C_6H_3Br \cdot CH(OH) \cdot CHBr \cdot CO_2H, C_{23}H_{26}O_4N_2$, was obtained as a vitreous residue by the evaporation of its alcoholic solution; but crystallisation set in when the amorphous mass was triturated, after a few days' keeping, with methyl alcohol. After this preliminary operation, crystallised brucine (39·5 grams) was added to a hot solution of one molecular proportion of the acid (30 grams) in methylated spirit (150 c.c.). It dissolved immediately, but on removing the solution from the water-bath and seeding it with the crystalline salt, rosettes of fine, colourless needles were slowly deposited (24·5 grams). At a concentration of 1 per cent. in 50 per cent. aqueous alcohol, these gave $[\alpha]_D - 14 \cdot 7°$. By slow recrystallisation from the last-named solvent, the salt was deposited in large, transparent prisms of high lustre. On repeating this process several times, fluctuations in specific rotatory power were noticed, but these were less pronounced than in the case of the brucine salt of cinnamic acid bromohydrin. The lowest numerical value observed was $[\alpha]_D - 12 \cdot 7°$ (Found : N = 3·7. $C_{30}H_{36}O_8N_2Br_2$ requires N = 3·7 per cent.).

The acid obtained from the last-named fraction by treatment with hydrochloric acid and extraction with ether was lævorotatory: 0·7138 gram, dissolved in absolute alcohol as noted above, gave $\alpha_D - 0 \cdot 51°$; whence $[\alpha]_D - 10 \cdot 7°$, and $M[\alpha]_D - 36 \cdot 9°$. The melting point was 148°. When dissolved in hot benzene containing a little alcohol and allowed to crystallise slowly, the acid was deposited in large, transparent prisms, and both the specific rotatory power and the melting point remained unaltered.

Of the two salts, l*AlB* and d*AlB*, the former is thus the less soluble in the example under notice. The two salts appeared to possess a tendency to form solid solutions, and the separation was further complicated by the production of an oily styrene derivative during the concentration of the mother-liquors on the water-bath. The highest numerical value of $[\alpha]_D$ observed for any crystalline separation was − 23·8°. The impure acid regenerated from the mother-liquor of this fraction was obtained from the ethereal extract as a partly crystalline mass, smelling of the styrene derivative; on washing out the oily impurity with a little benzene, the residual acid melted at 140—142°, and had $[\alpha]_D + 7 \cdot 4°$ in 4 per cent. absolute alcoholic solution. After recrystallisation from benzene containing a little alcohol, the melting point rose to 145° and the value of $[\alpha]_D$ to + 8·6°. A second recrystallisation gave a product melting at 148° and having $[\alpha]_D + 10 \cdot 7°$ in 4 per cent. absolute

alcoholic solution; whence $M[\alpha]_D + 36\cdot9°$. Both melting point and rotatory power were unaltered by further recrystallisation. As the highest values obtained for the dextro-acid are identical with those recorded above for the lævo-acid, and since the two preparations melted very definitely at the same temperature, it seems justifiable to conclude that the two enantiomerides were optically pure. The form assumed by the melting-point curve of their mixtures indicates that the partly compensated acids melt as mixtures of optically active and racemic compounds (Roozeboom, *Zeitsch. physikal. Chem.*, 1899, **28**, 508). The resolution was not facilitated by treating the externally compensated acid with half a molecular proportion of brucine. The cinchonine salt was not obtained crystalline.

5-*Bromo-2-methoxyphenylacetaldehyde,* $OMe\cdot C_6H_3Br\cdot CH_2\cdot CHO$.

A mixture of $\alpha:5$-dibromo-β-hydroxy-2-methoxy-β-phenylpropionic acid (30 grams) and water (150 c.c.) was heated on a boiling water-bath for thirty minutes with a solution of sodium hydroxide (6·8 grams in 20 c.c. of water). On the addition of a 25 per cent. solution of sulphuric acid (25 grams) to the warm liquid, carbon dioxide was evolved and a heavy yellow oil separated. The ethereal extract of this oil, when shaken with a saturated aqueous solution of potassium hydrogen sulphite, yielded a colourless, crystalline bisulphite compound (15·9 grams), which was collected, washed with ether, and decomposed with dilute sulphuric acid. The aldehyde was obtained by extraction with ether in the form of a viscous, pale yellow oil, which showed no tendency to crystallise after keeping for several months. When heated to 200°, it darkened, and at a somewhat higher temperature decomposed. The characteristic *semicarbazone,* $OMe\cdot C_6H_3Br\cdot CH_2\cdot CH\ddot{:}N\cdot NH\cdot CO\cdot NH_2$, was prepared by adding a warm alcoholic solution of the aldehyde (2 grams in 20 c.c.) to a solution of semicarbazide hydrochloride (2 grams) and sodium acetate (3 grams) in a little hot water. The mixed liquid was well shaken for about twenty minutes and then poured into water. The resulting white precipitate was sparingly soluble in boiling alcohol, from which it crystallised on cooling in rosettes of fine, colourless needles, melting at 185° (Found : $N = 14\cdot6$. $C_{10}H_{12}O_2N_3Br$ requires $N = 14\cdot7$ per cent.).

Summary.

1. Halogenohydrins have been prepared in almost quantitative yields by the action, under carefully regulated conditions, of cold dilute chlorine water, or bromine water, on free cinnamic acid.

2. By the interaction, under similar conditions, of methyl-coumarinic acid and bromine water, a closely corresponding amount of a mixture of two isomeric bromohydrins of the type

$$OMe·C_6H_3Br·CH(OH)·CHBr·CO_2H$$
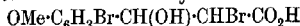
has been obtained. The crystalline constituent (m. p. 153—154°), isolated in 82·9 per cent. yield, has been shown to contain a nuclear bromine atom in the p-position to the methoxy-group : it has been resolved, with the aid of brucine, into two optically active components having $M[\alpha]_D \pm 36·9°$. The optical resolution of cinnamic acid bromohydrin has also been submitted to further examination, with interesting results.

3. No appreciable difference has been observed between methyl-coumarinic acid and methylcoumaric acid in their reaction with bromine water.

4. An improved method is indicated for the preparation of phenylacetaldehyde; and 5-bromo-2-methoxyphenylacetaldehyde has been made in a similar way.

5. Attempts to effect the direct addition of hypoiodous acid and of cyanic acid to cinnamic acid have proved unsuccessful.

We express our thanks to Messrs. L. A. Basser, B.Sc., and L. Cash, B.Sc., for preparing the methylcoumaric acid and methyl-coumarinic acid used in this work.

Further investigations in this and related fields are in progress.

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CCII.—The Application of Hofmann's Reaction to Substituted Phthalimides.

By Tom Sidney Moore, Muriel Tregarthen Marrack, and Annif Kathleen Proud.

THE work described in this paper was carried out to determine whether the application of Hofmann's reaction to substitution derivatives of phthalimide would serve for the preparation in quantity of certain substituted anthranilic acids required for other work; and since in each such reaction two isomeric, substituted anthranilic acids are to be expected, the opportunity was taken of determining the effect of the nature and position of the substituting group on the proportions of the two isomerides produced.

The main results are :

	Total yield per cent.	Proportion of products.
4-Chlorophthalimide	95	3 parts of 4-chloroanthranilic acid ; 1 part of 5-chloroanthranilic acid as anhydride.
4-Sulphophthalimide	Trace	Trace of 4-sulphoanthranilic acid ; no 5-sulphoanthranilic acid.
3-Acetylaminophthalimide...	55	2 parts of 6-acetylaminoanthranilic acid ; 1 part of 2-methylbenziminazole-4-carboxylic acid.

The reaction thus affords a convenient method for the preparation of 4-chloroanthranilic acid, and a possible method for 6-acetyl-aminoanthranilic acid.

The products obtained by similar treatment of 3- and 4-nitro-phthalimides have been already investigated by Seidel and Bittner (*Monatsh.*, 1902, **23**, 418) and by Kahn (*Ber.*, 1902, **35**, 471).

	Total yield per cent.	Proportion of products.
3-Nitrophthalimide	80	All 6-nitroanthranilic acid (Seidel and Bittner). Kahn finds a small quantity of 3-nitroanthranilic acid.
4-Nitrophthalimide	90	4 parts of 4-nitroanthranilic acid ; 1 part of 5-nitroanthranilic acid.

Thus in all these cases the derivative in which the amino-group takes up a *meta*-position with respect to the substituting group is produced in the larger quantity, irrespective of the nature of the group and of its position.

The behaviour of 3-acetylaminophthalimide with sodium hydroxide was unexpected. On attempting to estimate the amount of imidic nitrogen present by distilling with excess of alkali and absorption of the ammonia, two experiments gave 2·07 and 2·22 of imidic nitrogen, the theoretical value being 6·86 per cent. The same solution, after standing over-night, gave on distillation more ammonia, and by distilling every day for a week 85 per cent. of the theoretical amount of ammonia was obtained. The correct amount of ammonia was obtained at once if the substance was boiled with hydrochloric acid before the ammonia was distilled off.

Bogert and Jouard (*J. Amer. Chem. Soc.*, 1909, **31**, 483) find that when 3-acetylaminophthalimide is boiled with 5 per cent. potassium hydroxide, the solution on acidification gives 2-methyl-4-quinazol-one-5-carboxylic acid, and the formation and the subsequent slow decomposition of this compound in the presence of the strong

alkali we used offer a possible, if unlikely, explanation of the slow evolution of ammonia. But examination of the sodium salt isolated from the solution after 20 per cent. of the ammonia had been distilled off, and after 80 per cent. had been distilled off, showed that they were, at any rate mainly, sodium acetylamino-phthalamate and sodium acetylaminophthalate respectively. The fact that 3-acetylaminophthalimide undergoes reaction with alkali and sodium hypochlorite at much the same rate as phthalimide itself shows that the slow reaction recorded above cannot be due to slow formation of the salts of the two acetylaminophthalamic acids, since these are intermediate products in the reaction with sodium hypochlorite (Mohr, *J. pr. Chem.*, 1909, [ii], **80**, 1). It thus appears likely that the reaction, which is abnormally slow, is the action of alkali on the salts of the 3- and 6-acetylaminophthal-amic acids.

A similar slow reaction with alkali has been recorded by Kolbe (*J. pr. Chem.*, 1884, [ii], **30**, 475) in the case of the closely related compound, anthranilamide.

Experimental.

4-Chlorophthalic Acid.—The following method was found to give better yields and to be more convenient than that described by Egerer and Meyer (*Monatsh.*, 1913, **34**, 81). Almost theoretical yields of the acid sodium salt can be obtained by passing chlorine into a solution of 20 grams of phthalic anhydride (or the corresponding amount of the acid) in 200 c.c. of water containing 38·4 grams of sodium hydroxide until crystals are no longer deposited. The pure chlorophthalic acid is best obtained by adding the equivalent amount of dilute sulphuric acid to a solution of the twice-recrystal-lised acid sodium salt, extracting with ether, and recrystallising the residue after removal of the ether from benzene containing a few drops of glacial acetic acid. Both the acid and its salts retain small quantities of hydrochloric acid and chlorides with great tenacity, and we have never been able to obtain direct from aqueous solution products free from chloride. In any case, it is very difficult to get a specimen of 4-chlorophthalic acid in a condition for analysis. Thus the analysis of a specimen which had been dried in a vacuum for a week indicated that the substance still contained solvent (Found : Cl = 17·03. Calc., Cl = 17·70 per cent.); whilst on heating at 100° continuous loss of weight occurred owing to anhydride formation (Found : after heating for two hours at 100°, Cl = 19·41 per cent.). These observations explain the varying melting points and unsatisfactory analyses recorded by

earlier workers (Auerbach, *Jahresber.*, 1880, 862; Alén, *Bull. Soc. chim.*, 1881, [ii], **36**, 434; Claus and Dehne, *Ber.*, 1882, **15**, 321; Krüger, *Ber.*, 1885, **18**, 1759; Egerer and Meyer, *loc. cit.*).

4.*Chlorophthalimide.*—This compound, prepared through the anhydride in the usual way, was allowed to react with sodium hypochlorite under the condition ordinarily used for phthalimide (Eng. Pat. 18246, 1890; *J. Soc. Chem. Ind.*, 1891, **10**, 831). The greater part of the product was precipitated from the alkaline solution left after the reaction on acidification with acetic acid, and a small quantity (about one-tenth of the whole) obtained by addition of copper acetate and subsequent decomposition of the precipitated copper salt with hydrogen sulphide. The total yield was 95 per cent. of the theoretical.

Extraction of the product with light petroleum (b. p. 92—102°) left a residue, m. p. 220°, which, after one recrystallisation from glacial acetic acid, melted at 235—236° and was unaltered by subsequent recrystallisation. This residue formed 80 per cent. of the product obtained by precipitation with acetic acid and 30 per cent. of the product obtained from the copper salt. On distillation with soda-lime, it gave an oil of which the acetyl derivative was identified as *m*-chloroacetanilide. The compound, therefore, is 4-chloroanthranilic acid, for which Cohn (*Monatsh.*, 1901, **22**, 481) also found the m. p. 235—236° (Found: Cl = 20·62. Calc., Cl = 20·70 per cent.).

From the residues left on evaporating the petroleum extracts, an almost white product crystallising in short, white needles, shrinking at 172° and melting at 178—179°, was obtained by fractional crystallisation from benzene and final crystallisation from glacial acetic acid. The substance is soluble in sodium carbonate solution, contains a primary amino-group, and gives *p*-chloroaniline on distillation with lime. The melting point does not agree with either of those given for the expected product, 5-chloroanthranilic acid, namely, 145—148° (Hübner, *Annalen*, 1865, **135**, 111) and 211—212° (Freundler, *Bull. Soc. chim.*, 1907, [iv], **1**, 225). The anhydride, $CO_2H \cdot C_6H_3Cl \cdot NH \cdot CO \cdot C_6H_3Cl \cdot NH_2$, of 5-chloroanthranilic acid would have the properties of our compound and the same chlorine content (Found: Cl = 22·08. Calc., Cl = 21·85 per cent.), but time and material to establish the identity were wanting.

3.*Acetylaminophthalimide.*—This compound was prepared by the direct acetylation of 3-aminophthalimide, which itself is best obtained by reduction of 3-nitrophthalimide * with stannous

* It does not seem to have been recorded that 3-nitrophthalic acid, several specimens of which we examined, crystallises from aqueous solution with two

chloride in the cold (Bogert and Jouard, *J. Amer. Chem. Soc.*, 1909, **31**, 483).

The behaviour of this substance with sodium hydroxide has already been described (p. 1787). The salt obtained from the alkaline mother-liquor after 20 per cent. of the theoretical quantity of ammonia had been evolved gave, after recrystallisation from water and drying to constant weight, $N = 11·25$; $Na = 9·53$. $CO_2Na·C_6H_3(CO·NH_2)·NH·CO·CH_3$ requires $N = 11·48$; $Na = 9·45$ per cent. This salt gave ammonia when heated with soda-lime.

From the mother-liquor obtained by heating the imide with sodium hydroxide until 80 per cent. of the ammonia had been evolved, a sodium salt was obtained which gave, after similar treatment, $N = 5·10$; $Na = 17·11$. $(CO_2Na)_2C_6H_3·NH·CO·CH_3$ requires $N = 5·24$; $Na = 17·23$ per cent.

The conditions used for the reaction of sodium hypochlorite with 3-acetylaminophthalimide were the same as those for 4-chloro-phthalimide. From the resulting solution both copper and barium salts may be precipitated, but these are apparently complex compounds, for they are not decomposed by hydrogen sulphide and sulphuric acid respectively. The solution was nearly neutralised with hydrochloric acid, allowed to evaporate to a small bulk, and acidified with concentrated hydrochloric acid. After filtration from a small quantity of tarry matter, the solution was allowed to evaporate to dryness, and the organic matter dissolved out of the residue with absolute alcohol. Fractional crystallisation of the alcoholic solution separated the product into two substances.

The less soluble fraction consisted of small, pale brown crystals easily soluble in methyl or ethyl alcohol, moderately soluble in water, and insoluble in ether, benzene, or chloroform. It remained unmelted at 300°, contained nitrogen, but no amino-group, and was soluble in sodium carbonate solution (Found : $N = 15·42$. $C_9H_8O_2N_2$ requires $N = 15·71$ per cent.).

The substance thus appears to be 2-methylbenziminazole-4-carboxylic acid, which might be expected to be formed from 3-acetylaminoanthranilic acid, one of the possible products of the reaction with sodium hypochlorite. On distillation with soda-lime, it gave a product agreeing in all its properties with a specimen of 2-methylbenziminazole obtained by the reduction of *o*-nitro-acetanilide.

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molecules of water, which it loses at 110° (Found : $N = 5·65$. $C_9H_5O_6N,2H_2O$ requires $N = 5·67$ per cent.). The anhydrous acid melts at 218°, as does also the hydrated acid when heated slowly. But immersed in a bath at 200°, the hydrated acid melts and re-solidifies (compare Miller, *Annalen*, 1881, **208**, 224; Bogert and Boruschek, *J. Amer. Chem. Soc.*, 1901, **23**, 740).

The second fraction was darker in colour and more soluble in water and the alcohols than the derivative described above, but similarly insoluble in other solvents. It does not melt below 300°, contains a primary amino-group, and is soluble in alkaline solution. On distillation with lime, acetyl-m-phenylenediamine was obtained (Found : N = 14·45. $C_9H_{10}O_3N_2$ requires N = 14·43 per cent.).

The substance is thus the expected 6-acetylaminoanthranilic acid.

4-*Sulphophthalimide.*—Rée (T., 1886, **49**, 518) prepared the ammonium salt of this compound by heating the diammonium salt of 4-sulphophthalic acid at 190°. We find that on passing dry ammonia into 4-sulphophthalic acid while the temperature is gradually raised to 190°, and maintaining the mass at that temperature until no more ammonia shall be evolved—three to four days—a substance easily soluble in water to give an acid solution and containing the proper percentage of nitrogen for the imide will be obtained (Found : N = 6·16. Calc., N = 6·17 per cent.).

This method of preparation might lead, not only to the desired 4-sulphophthalimide, but also to the isomeric sulphonamide of phthalic anhydride, $NH_2 \cdot SO_2 \cdot C_6H_3 < ^{CO}_{CO} > O$. But from the ease with which ammonia is liberated from the product in alkaline solution we conclude that the substance cannot contain the very stable sulphonamide group, and that it is therefore 4-sulpho-phthalimide.

The product of the reaction of this substance with sodium hypochlorite was almost entirely the salt of 4-sulphophthalic acid, but by fractional crystallisation a very small quantity of a substance giving the reactions of an aminosulphonic acid, which was soluble in water with a blue fluorescence, was obtained. Since, according to Kalle & Co. (D.R.-P. 138188, 1903), Hollemann (*Rec. trav. chim.*, 1905, **24**, 194) and Kastle (*Amer. Chem. J.*, 1911, **45**, 58), 4-sulphoanthranilic acid and its salts show such a fluorescence in dilute solution, and this acid is one of the possible products, whilst no observation of fluorescence of the other possible product, 5-sulphoanthranilic acid, is recorded in the literature, we conclude that a small amount of the former substance was produced.

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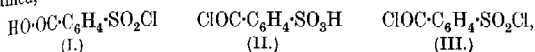
CCIII.—m-*Dithiobenzoic Acid.*

By Samuel Smiles and Jessie Stewart.

THE behaviour of *o*-dithiobenzoic acid in sulphuric acid solution has been the subject of previous investigations (T., 1910, **97**, 1290; 1911, **99**, 640; 1912, **101**, 572; 1915, **107**, 1377). Extending this study to other aromatic disulphides, attention was first directed to the *meta*-isomeride. Preliminary experiments with this substance showed that the type of condensation which it undergoes is somewhat different from those observed with the *ortho*-disulphide, and before proceeding further it was necessary to prepare considerable quantities of the acid. The methods at present available for this purpose start either with *m*-aminobenzoic acid, which is converted to the sulphinic acid (Gattermann, *Ber.*, 1899, **32**, 1151), this being finally reduced to the mercaptan, or from *m*-sulpho-benzoic acid (Frerichs, *Ber.*, 1874, **7**, 793), from which the dichloride is prepared before reduction of the sulphonic group can be effected. On applying these methods, it was found that for various reasons neither is suitable to the economical preparation of large quantities of the desired material.

A few observers have recorded the production of sulphonyl chlorides by the action of chlorosulphonic acid on aromatic compounds. The cases of benzene- and the toluene-sulphonyl chlorides (*Ber.*, 1909, **42**, 1802, 2057; Harding, this vol., p. 1261) have been thoroughly investigated; other examples are those of *m*-nitrobenzenesulphonyl chloride (D.R.-P. 89997, 1896) and the sulphonyl chloride of *o*-nitrophenol (*Zeitsch. angew. Chem.*, 1920, **33**, 8). These cases, however, appear to be exceptional; in fact, the formation of the sulphonic acid appears usually to have been observed in the action of this reagent. We find, however, on employing suitable conditions, of which the most important is the use of an excess of the reagent, that benzoic acid yields 90—95 per cent. of *m*-chlorosulphonylbenzoic acid. By reduction of this product, *m*-thiolbenzoic acid, is readily prepared and thence the required *m*-dithiobenzoic acid is obtained by the usual method of oxidation. Since the sulphonyl chlorides are a very convenient source of most other sulphur derivatives, the investigation of this reaction is being extended to other types of aromatic compound, and it has been found that many of these yield the sulphonyl chloride when treated with chlorosulphonic acid under suitable conditions.

For the product obtained from benzoic acid and chlorosulphonic

acid either of two alternative structures (I or II) might be entertained,

$$HO \cdot OC \cdot C_6H_4 \cdot SO_2Cl \qquad ClOC \cdot C_6H_4 \cdot SO_3H \qquad ClOC \cdot C_6H_4 \cdot SO_2Cl,$$
$$\text{(I.)} \qquad\qquad\qquad \text{(II.)} \qquad\qquad\qquad \text{(III.)}$$

but the latter must be rejected, since the substance on reduction yields the corresponding mercaptan. The situation of the carboxyl and sulphonic groups follows from the fact that the chloride (I) and sulphonamide are identical with the corresponding substances prepared from m-sulphobenzoic acid. When the liquid dichloride (III) of m-sulphobenzoic acid is submitted to hydrolysis by cold water, a solid monochloride is obtained, and it has been considered doubtful whether this product is the sulphonyl or the carboxyl chloride (I or II) (Limpricht and Uslar, *Annalen*, 1858, **106**, 30). The substance is identical with that now obtained directly from benzoic acid with chlorosulphonic acid, and is therefore the chlorosulphonyl derivative (I). Sulphonation of benzoic acid with sulphuric acid under certain conditions yields a small quantity of the *para*-isomeride (Remsen, *Annalen*, 1875, **178**, 278), but this substance has not been detected in the product from chlorosulphonic acid under the conditions adopted.
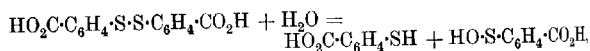
m-Dithiobenzoic acid in most of its reactions resembles other disulphides, but it is very readily attacked by cold dilute aqueous alkali hydroxide, and this exceptional behaviour has led to a more detailed study of the substance. If the acid be directly titrated with alkali, the value obtained for the equivalent will be normal; but if it be dissolved in excess of cold alkali and the amount of the latter uncombined be then estimated, it will be found that more than two equivalents of alkali hydroxide have been utilised by a molecular proportion of the acid. The reaction which takes place is progressive, and its speed depends on the temperature, the concentration, and on the relative amount of the alkali hydroxide employed. The circumstances are best illustrated by data obtained with solutions at the atmospheric temperature containing six molecular proportions of potassium hydroxide of different concentrations to one proportion of disulphide. The figures quoted represent the number of equivalents of alkali hydroxide which had been employed in reaction with one molecular proportion of the acid after the solution had been kept for the stated periods before titration with hydrochloric acid.

	0 (mins.).	30.	60.	2 (days).	3.	6.
0·1N·Potassium hydroxide ...	2·38	2·75	3·0	—	—	4·0
0·2N. " " ...	2·47	3·5	3·7	—	4·0	—
0·5N· " " ...	3·26	3·6	3·75	4·0	—	—
N. " " ...	3·31	3·65	3·8	—	4·0	—

Examination of the products shows that simultaneous oxidation and reduction take place with rupture of the disulphide system. The chief product is m-thiolbenzoic acid; in fact, this substance is readily prepared by acidifying the strongly alkaline solution after it has been kept for a short time. The product or products of oxidation are not so easily recognised, the only one which has been isolated is the disulphoxide, $(-SO \cdot C_6H_4 \cdot CO_2H)_2$.

The interaction of alkali hydroxide and aromatic disulphides has previously been noticed in the cases of the diphenyl (Schiller and Otto, *Ber.*, 1876, **9**, 1637; Fromm, *Ber.*, 1908, **41**, 3403) and the di-p-nitrophenyl (Fromm, *ibid.*, 1908, **41**, 2267) derivatives. With these substances the reaction was effected by boiling alcoholic solutions of alkali hydroxide, the cold medium having no effect. The products isolated were the corresponding mercaptans and small quantities of the sulphinic acids or their simple derivatives. With the use of the boiling alcoholic reagent, the nature of the reaction is not at all clear, for it is difficult to determine whether or not the formation of mercaptan is due to reduction by this reagent. In the case of m-dithiobenzoic acid, where interaction is effected by the cold dilute aqueous reagent, the conditions are simpler.

The formation of the thiol derivative from the disulphide indicates that rupture of the dithio-system has taken place, and since it cannot be supposed that under these conditions the change is due to direct reduction by any reagent present, it must be assumed that the process is primarily one of hydrolysis which is effected by the alkali hydroxide. In fact, no simpler explanation can be given than that represented by the equation

$$HO_2C \cdot C_6H_4 \cdot S \cdot S \cdot C_6H_4 \cdot CO_2H + H_2O = \\ HO_2C \cdot C_6H_4 \cdot SH + HO \cdot S \cdot C_6H_4 \cdot CO_2H,$$

in which the mercaptan and sulphenic acid are the primary products. This type of decomposition has been shown to occur with disulphides in sulphuric acid solution, and it has been previously suggested to explain various reactions of substances containing the dithio-group. Attempts to isolate a derivative of the sulphenic acid in the form of an alkyl sulphoxide were not successful, the action of methyl sulphate with the alkaline solution yielding only the m-methylthiolbenzoic acid. This result is scarcely surprising in view of the instability of the sulphenic acids and their derivatives. Zincke (*Annalen*, 1912, **391**, 57; 1913, **400**, 1; 1914, **406**, 106) has shown that these substances undergo spontaneous decomposition even in the presence of alkali, yielding disulphides, disulph-oxides, and sulphinic acids. Search for the last-named two

derivatives showed that the benzoic acid m-disulphoxide was formed in small quantity; but the sulphinic acid was not isolated either as such or as the methyl sulphoxide after alkylation of the reacting mixture. It is worth notice that boiling aniline or pyridine attacks the disulphide in the same manner as alkali hydroxide.

It seems impossible to give any definite expression to the reaction beyond the primary hydrolytic change represented in a foregoing paragraph. There is little doubt that the secondary decomposition which appears to give rise to the oxidation products is a complicated process leading to other substances together with the disulphoxide. m-Thiolbenzoic acid, which is the chief product of this reaction, may, like other mercaptans, be oxidised to the disulphide. Hence, if there be added to the alkaline reacting mixture some reagent which will reconvert the mercaptan as it is formed to the original disulphide, the latter should be completely converted to the disulphoxide and other subordinate products of the secondary decomposition. Experiments made with iodine confirm this view, good yields of the disulphoxide being obtained.

In this behaviour with cold aqueous alkali, m-dithiobenzoic acid is exceptional; other aromatic disulphides which do not contain the acid group appear to be unattacked by the reagent. The patented process (D.R.-P. 193800, 1906) for the preparation of o-methylthiolbenzoic acid by heating the dithio-acid with alkali and methyl sulphate appears to indicate that the *ortho*-isomeride behaves like the *meta*-compound. Experiments made under conditions comparable with those described in a former paragraph show that the reaction does take place, but much more slowly. For example, at atmospheric temperature with six equivalents of $0.84N$-potassium hydroxide to one molecular proportion of o-dithiobenzoic acid, after one hour 2.0, after nineteen hours 2.7, and after forty-eight hours 2.95 equivalents of alkali had entered into reaction. The behaviour of other disulphides is being investigated.

E X P E R I M E N T A L.

m-Chlorosulphonylbenzoic Acid, $CO_2H \cdot C_6H_4 \cdot SO_2Cl.$

(1) A mixture of benzoic acid and five molecular proportions of chlorosulphonic acid was heated at 125° for one hour in an oil-bath; the evolution of hydrogen chloride had then ceased. The cooled product was poured over crushed ice, and the solid mass ground under ice-cold water, collected, washed with water, and finally dried in a vacuum. The crude sulphonyl chloride melted at about 122°, and after recrystallisation from benzene the pure

material was obtained in colourless prisms melting at 131° (Found: Cl = 16·0; S = 14·3.   Calc., Cl = 16·1; S = 14·4 per cent.).

The corresponding sulphonamide was prepared by the action of dilute aqueous ammonia on the chloride. It was recrystallised from a mixture of acetone and water and formed colourless prisms which melted at 233°.

(2) *m*-Chlorosulphonylbenzoyl chloride was prepared from the sodium salt of *m*-sulphobenzoic acid and phosphorus pentachloride (Limpricht and Uslar, *Annalen*, 1857, **102**, 250). The liquid product was mixed with excess of water and set aside. After the lapse of ten days it had become converted to a colourless, crystalline mass. This was collected and recrystallised from benzene; the product melted at 131° and was identical with that obtained from benzoic acid as described in the foregoing paragraph. The corresponding amide was also identical with that prepared from *m*-chlorosulphonylbenzoic acid.

m-*Dithiobenzoic Acid*, $(HO_2C \cdot C_6H_4 \cdot S-)_2$.

Thirty-five grams of zinc dust were added in small quantities from time to time to a solution of 20 grams of *m*-chlorosulphonyl-benzoic acid in 150 c.c. of alcohol and 100 c.c. of concentrated hydrochloric acid. The liquid was constantly shaken during the addition, which extended over six hours. Undissolved zinc and a colourless solid (*a*) were collected from the mixture. The clear liquid was mixed with solid ferric chloride, when the required disulphide was precipitated in the crystalline state. This was collected, washed with water and then with acetone before recrystallisation from acetic acid. The product formed cream-coloured aggregates of needles which melted at 246° (Found : C = 54·5; H = 3·6; S = 20·7.   Calc., C = 54·9; H = 3·3; S = 20·9 per cent.). Gattermann (*loc. cit.*) gives the melting point of this substance as 242°. *m*-Dithiobenzoic acid is insoluble in water and sparingly soluble in most organic solvents. The solution in sulphuric acid becomes green on agitation with benzene, forming condensation products which are now under investigation. The yield of crude material was about 65—67 per cent. of the theoretical. A further small amount may be obtained from the zinc derivative of *m*-thiol-benzoic acid (*a*) which separates during the reduction. In this process esterification takes place to a certain extent, and a small quantity of ester may be obtained by the addition of water after the removal of the dithiobenzoic acid. The presence of this substance is apt to render purification of the acid difficult, and experiments were made using acetic acid as the solvent in reduction,

but the yields, being in the neighbourhood of 35 per cent., were much poorer than that obtained with alcohol as the solvent.

m-*Thiolbenzoic Acid*, $SH \cdot C_6H_4 \cdot CO_2H$.

This compound may be prepared by reduction of the disulphide in the usual manner; it is also formed by the interaction of alkali hydroxide with *m*-dithiobenzoic acid. The latter substance was dissolved in excess of aqueous $2N$-sodium hydroxide. The solution was kept for two hours at $18°$ and then mixed with excess of dilute sulphuric acid. The copious precipitate was collected and recrystallised from a mixture of alcohol and water, when *m*-thiolbenzoic acid was obtained in needles melting at $146—147°$. The substance was converted by ferric chloride to the disulphide, and its properties agreed with those already assigned to the substance.

m-*Methylthiolbenzoic Acid*, $SMe \cdot C_6H_4 \cdot CO_2H$.

A solution of 20 grams of *m*-dithiobenzoic acid in excess of N-sodium hydroxide was shaken for three hours with two molecular proportions of methyl sulphate. The small quantity of oil which separated during the process was removed by extraction with ether, then the aqueous solution was acidified with dilute sulphuric acid. Ten and a half grams of *m*-methylthiolbenzoic acid were obtained. After recrystallisation from a mixture of alcohol and water, the substance formed feathery needles which melted at $126—127°$ (Found: $C = 56.8$; $H = 5.0$; $S = 18.9$. $C_8H_8O_2S$ requires $C = 57.1$; $H = 4.76$; $S = 19.0$ per cent.). Thorough search for the sulphoxide or for the sulphone $C_6H_4(CO_2H) \cdot SO_2 \cdot CH_3$ which would have indicated the formation of a sulphinic acid during this reaction, was without success.

m-*Methylsulphonebenzoic acid*, $HO_2C \cdot C_6H_4 \cdot SO_2 \cdot CH_3$, was prepared in the course of this examination by oxidising the methylthiol with permanganate in glacial acetic acid solution. The substance crystallised in shining leaflets on cooling the hot aqueous solution; it melted at $230°$ (Found: $C = 47.7$; $H = 4.2$; $S = 16.0$. $C_8H_8O_4S$ requires $C = 48.0$; $H = 4.0$; $S = 16.0$ per cent.).

Benzoic Acid m-*Disulphoxide*, $(HO_2C \cdot C_6H_4 \cdot SO)_2$.

The preparation of this substance is best effected by the action of iodine on an aqueous alkaline solution of the disulphide. A cold solution of 5 grams of the disulphide in excess of N-potassium hydroxide was treated with four atomic proportions of iodine. A solution of the latter in potassium iodide was slowly added from

time to time, more alkali being added when necessary to preserve alkalinity of the solution. When all the iodine had been added, the liquid was mixed with excess of dilute sulphuric acid and set aside. After the lapse of a few days, 3·8 grams or a yield of 69 per cent. of benzoic acid m-disulphoxide had separated. The substance is readily soluble in hot alcohol, and when recrystallised from this medium it was obtained in small, white needles melting at 220°. The ferric salt, like that of the disulphide, is insoluble in water and soluble in dilute mineral acids. When the solution in sulphuric acid is mixed with a drop of phenetole, a blue colour is slowly developed, hydrolysis to the sulphinic acid then setting in (Hilditch, T., 1911, **99**, 1091) (Found : C = 49·5; H = 3·1; S = 19·1. $C_{14}H_{10}O_6S_2$ requires C = 49·7; H = 2·98; S = 18·93 per cent.). This disulphoxide is also formed by the interaction of the disulphide and cold alkali hydroxide. It may be obtained in small quantity by setting aside the filtrate from the m-thiolbenzoic acid described in a foregoing paragraph. The substance then separates in a somewhat impure condition. It was obtained in better yield by boiling the solution of the disulphide in pyridine for one hour. The cold liquid was incompletely neutralised with dilute sulphuric acid, and, after the precipitated disulphide had been removed, the solution was rendered strongly acid. It was then repeatedly extracted with ether, and when this was evaporated the residual oil solidified. The product consisted of the somewhat impure disulphoxide. Similar results were obtained with boiling aniline, but the yields of disulphoxide were even smaller.

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CCIV.—*The Rate of Hydrolysis of Methyl Acetate by Hydrochloric Acid in Solutions containing Sucrose.*

By GEORGE JOSEPH BURROWS.

THE influence of sucrose on the rate of hydrolysis of esters by acids has been studied by various investigators. The results obtained by Henri and Larguier des Bancels (*Compt. rend. Soc. Biol.*, 1901, **53**, 784) indicate that sucrose has a slightly accelerative effect on the rate of hydrolysis of methyl acetate. Coppadoro (*Gazzetta*, 1901, **31**, i, 425) concluded that the addition of sucrose had no apparent effect, whilst, more recently, Griffith, Lamble, and Lewis

(T., 1917, **111**, 389) have stated that it diminished the rate of hydrolysis of the ester. The results recorded in the present paper were obtained during an investigation of the influence of various substances on the rate of hydrolysis of esters by acids; they are comparable with those of Griffith, Lamble, and Lewis, nevertheless the author considers that they indicate that sucrose has an accelerative effect.

The subject is of interest in view of the fact that both the ester and the sucrose are being hydrolysed by the acid at the same time.

In all the experiments the temperature was 25°. The solutions in which no sucrose was present were prepared by dissolving the required amount of methyl acetate in water, adding the correct quantity of standard hydrochloric acid, and diluting with water to 100 c.c. (at 25°). In the case of solutions containing sucrose, unless otherwise stated, the latter was added to the solution before diluting to the final volume. The reaction was followed in the usual way by estimating the amount of acetic acid produced by the hydrolysis of the ester after various intervals of time.

The velocity constant k was calculated from the equation :

$$k = \frac{1}{t} \log_{10} \frac{\xi}{\xi - x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where ξ is the amount of ester hydrolysed when equilibrium has been attained, and x is the amount hydrolysed in time t (minutes). The values of k were found to be constant for the fraction of the reaction studied.

The equation from which k is calculated is obtained from $\frac{dx}{dt} = k(a - x)$, in which a is the initial concentration of ester. The correct equation for the rate of hydrolysis can be deduced only by considering the reaction as bimolecular and by taking the reverse reaction into account; thus :

$$\frac{dx}{dt} = k_1(b - x)(w - x) - k_2 x^2$$

where k_1 is the rate of hydrolysis, k_2 is the rate of esterification, b is the initial concentration of methyl acetate in gram-mols. per 1000 c.c. of solution, w is the initial concentration of water, and x is the number of gram-mols. of ester hydrolysed in t minutes.

From this is deduced by integration (Griffith and Lewis, T., 1916, **109**, 69),

$$k_1 = \frac{1}{tA} \log \frac{A + y + 2(K - 1)x}{A - y - 2(K - 1)x} \cdot \frac{(A - y)}{(A + y)} \quad . \quad . \quad . \quad (2)$$

where $\qquad K = \dfrac{k_2}{k_1} = \dfrac{C_{\text{ester}} \times C_{\text{water}}}{C_{\text{acetic acid}} \times C_{\text{alcohol}}}$ at equilibrium,

$$y = w + b, \text{ and } A = \sqrt{y^2 + 4(K-1)wb}.$$

For the solutions considered in this work, K varies only to a small extent. For the purpose of the present investigation, the rate of hydrolysis may be calculated, therefore, from the equation

$$k_c = \frac{1}{tw} \log \frac{\xi}{\xi - x} \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

so that the values $k_c = k/w$ are considered to represent the rates of hydrolysis of the ester after correcting for the differences in the initial concentrations of water in the various solutions. In this way, the following results (Table I) were obtained for the rates of hydrolysis of 5 per cent. methyl acetate solutions by $N/2$-hydrochloric acid in the presence of various amounts of sucrose.

TABLE I.

Experiment.	Sucrose per cent.	$k \times 10^4$.	w.	$k_c \times 10^6$.
1	0	14·97	52·32	28·6
2	7·5	16·6	49·60	33·5
3	15·0	17·5	46·88	37·3

This increase in the value of k_c may, at first sight, appear to be due to the increase in the concentration of the hydrochloric acid relative to that of the water, resulting from the decrease in the amount of water in the solution. The rate of hydrolysis was therefore determined for a solution containing the same amounts of water, ester, and hydrochloric acid as in the first experiment, to 100 c.c. of which, however, 7·5 grams of sucrose had been added. The mean value of k for this solution was found to be $15·6 \times 10^{-4}$, a value slightly greater than that obtained in experiment 1, although the catalyst had been diluted in the ratio $100 : 105$ owing to the increase in the volume produced by the added sucrose. Correcting for this dilution, the value $16·4 \times 10^{-4}$ is obtained. In order to obtain the corresponding value of k_c in this case, it is also necessary to correct for the dilution of the water. Whereas in experiment 1, 52·32 gram-molecules of water were present in 1000 c.c. of the solution, in the other case the same amount was present in 1050 c.c. The value of w is therefore $52·32/1·05$, whence $k_c = 32·9 \times 10^{-6}$. This value is considered to be strictly comparable with k_c for a solution containing no sucrose, and it agrees very closely with that obtained in experiment 2, with a solution prepared in such a way that its volume was 100 c.c. This result indicates that the presence

of sucrose increases the rate of hydrolysis of methyl acetate by about 17 per cent. for the particular concentrations used.

Similar accelerative effects were observed for the addition of sucrose to other concentrations of acid. These results are collected in Table II. In every case the total volume of the solution was 100 c.c., and it contained originally 5 per cent. of methyl acetate.

TABLE II.

Experiment.	Concentration of acid.	Sucrose per cent.	$k \times 10^4$.	w.	$k_c \times 10^6$.
4	$N/4$	0	7·16	52·35	13·63
5	,,	7·5	8·05	49·83	16·16
6	$N/8$	0	3·50	52·67	6·64
7	,,	7·5	3·99	49·95	7·99

It will be seen that the presence of sucrose increases the rate of hydrolysis of the ester in both the above cases, the effect increasing slightly with decreasing concentration of the acid.

For the hydrolysis of a 2 per cent. methyl acetate solution by $N/10$-trichloroacetic acid at 35°, Griffith, Lamble, and Lewis (loc. cit.) obtained the value $k = 1·572 \times 10^{-3}$, and for a similar solution to which, however, 8 grams of sucrose had been added, $k = 1·602 \times 10^{-3}$, results which compare with those given in the present paper. These authors then determined the rate of hydrolysis in a solution containing the same amounts of acid and water, but an amount of ester equal in volume to the total volume of ester and sucrose used in their previous experiment, and obtained the result $k = 1·77 \times 10^{-3}$. They state that this figure is directly comparable with the value $1·602 \times 10^{-3}$ obtained for the solution containing sucrose, and conclude that sucrose has a depressing effect.

It is well known that the rate of hydrolysis of an ester is not independent of the initial concentration, but increases with increasing concentration of the ester. This increase has been attributed to the corresponding decrease in the concentration of the water, the latter being considered to have an anti-catalytic effect in such reactions. It is this fact which renders it difficult to study the actual effect of a solute on the rate of hydrolysis of an ester, apart from that due to the change in the concentration of water. When a portion of the water is replaced by sucrose or other substance, one would expect a certain increase in the rate of the reaction resulting from this cause alone. At the same time, the present author considers that Griffith, Lamble, and Lewis have not established their conclusion that sucrose has a depressing effect on the rate of hydrolysis of methyl acetate; at the most, they can only conclude that it has a smaller accelerative effect than the addition

of the same volume of methyl acetate to the reaction mixture. Even this, however, has been found not to be the case in the present investigation, in which hydrochloric acid has been used as the catalyst.

The effect of increasing the initial concentration of the ester is shown by the results in Table III, for the rates of hydrolysis of various solutions of methyl acetate by $N/2$-hydrochloric acid.

TABLE III.

Experiment.	Initial concentration of ester per cent.	$k \times 10^4$.	w.	$k_c \times 10^6$.
8	2·5	14·81	53·72	27·6
9	5·0	14·97	52·32	28·6
10	10·0	15·94	49·60	32·1

The value of k_c for a solution containing initially 5 c.c. of ester and 5 c.c. of sucrose ($k_c = 33·5 \times 10^{-6}$) is greater than that for a solution containing 10 c.c. of methyl acetate. These results indicate that the rate of hydrolysis of the ester is increased to a greater extent by adding sucrose than by adding a further quantity of ester equal in volume to that of the sucrose.

Finally, the conclusion that sucrose has a definite accelerative effect is further supported by comparing the results given above with that obtained for a solution in which part of the water is replaced by an indifferent substance such as acetone. The rate of hydrolysis of 5 per cent. methyl acetate by $N/2$-hydrochloric acid in aqueous acetone solution containing 20 per cent. of acetone by volume was found to be $14·03 \times 10^{-4}$. In this case $w = 42·46$, whence $k_c = 33·0 \times 10^{-6}$. The corresponding value of k_c for a solution containing 5 per cent. of acetone by volume is $29·1 \times 10^{-6}$, which is smaller than the value for a solution containing 5 per cent. of sucrose by volume. It follows that the increase observed for a solution containing sucrose cannot be attributed entirely to a decrease in the total amount of water in the solution.

CCV.—The Dimorphism of Potassium Ethyl Sulphate.

By DALZIEL LLEWELLYN HAMMICK and JOHN MYLNE MULLALY.

IT was noticed by one of us (J. M. M.) that potassium ethyl sulphate is dimorphous. On crystallisation from methylated alcohol, the substance first appeared in tufts of long, feathery crystals, which,

as the solution cooled, redissolved and gave place to the ordinary foliated form. The same dimorphic change was observed after crystallisation from water. In this case, however, the change was suspended for twenty-four hours, the preparation being left untouched and protected from dust. On exposing the mass of crystals to the air, the transformation immediately started at several nuclei and was complete in a few minutes.

In order to show that the change is not one of hydration, the solid phase stable at low temperatures (the α-form) was analysed : 0·5050 gram was heated strongly in a platinum crucible with a few drops of concentrated sulphuric acid until no further decrease in weight occurred. The residue of potassium sulphate weighed 0·2682 gram. Since 0·5050 gram of potassium ethyl sulphate is theoretically equivalent to 0·2680 gram of potassium sulphate, the α-potassium ethyl sulphate cannot be hydrated. This result agrees with the previously published descriptions. Now the β-form can be obtained from the α by crystallisation from absolute alcohol or water, or by merely heating when dry. Hence the β-form must be anhydrous also.

For these and all following experiments the potassium ethyl sulphate was used only after being crystallised from alcohol, and dried in a vacuum over calcium chloride. It was then almost pure, containing only a trace of carbonate.

We are indebted to Mr. T. V. Barker for the following account of the modification stable at higher temperatures :

"The higher-temperature modification crystallises in needles with straight extinction, and therefore probably belongs to the orthorhombic system. The faster ray (that is, that with the greater refractive index) vibrates along the axis of elongation.

"The crystals belonging to the previously known monoclinic form are rhombs of about 93° and exhibit diagonal extinction. This is in full agreement with the published description." (See Groth, "Chemische Krystallographie," vol. III, p. 120).

The solubility curves were determined in order to find the transition point. The method used was that of Hartley and Thomas (T., 1906, **89**, 1013).

Known weights of potassium ethyl sulphate (1 to 2·5 grams) mixed with various amounts of water were heated in sealed tubes (see Fig. 1) placed in a bath the temperature of which could be altered at will and read with a standardised thermometer. The last few crystals to dissolve were watched with a lens in order to see whether their edges were rounded (indicating that they were dissolving) or sharp (growing). The required temperature of saturation was then the mean between the highest at which they were seen to

3 Q*

grow and the lowest at which they dissolved. It was easy to see
which was the solid phase in equilibrium with the
solution at different temperatures. Hence the two
corresponding solubility curves were obtained intersect-
ing at the transition point, which could only be found
thus to be in the neighbourhood of 50°.

FIG. 1.

By dissolving the last trace of solid and then cooling
the tube carefully, it was possible to crystallise the
β-form at temperatures at which the α was the more
stable. Hence a metastable solubility curve was obtained
for the β-form. No matter at what temperature crystal-
lisation took place, the β-form was always the first to
separate out, and at low temperatures it was much less
liable to change to the stable form than at higher ones
near the transition point. Great supersaturation of
both forms also occurred. In order therefore to induce
crystallisation or transformation in the tubes, a small
crystal for seeding was placed in the small pocket blown
on the stem of the tube (Fig. 1).*

The tubes were cleaned before use by washing with
acid, steaming for several hours, and then drying.

The data from which the curves were constructed
are as follows :

Percentage of KC$_2$H$_5$SO$_4$ in the solution.	Solution temperature for α-form.	Solution temperature for β-form.
49·5	−4·5°	−13·5°
51·946	−1·9	—
58·81	+8·7	− 5·2
66·6	21·1	+12·1
70·015	26·6	20·1
75·29	35·0	32·0
75·675	35·9	32·6
77·99	39·9	38·2
80·084	45·5	45·0
82·04	51·14	51·10
84·44		59·46
84·52		60·46
85·47		65·8
86·23		69·1
87·945		81·3
89·62		91·2

These points when plotted give the curves shown in Fig. 2. The
metastable curves are dotted.

The transition point was more accurately determined by the
thermometric method. The solid potassium ethyl sulphate was
mixed with a small quantity of water contained in a jacketed tube

* This device was suggested by General H. B. Hartley.

immersed in a water-bath. Both substance and bath were stirred and well-marked arrests in the former's temperature were observed at 51·4°, 51·6°, 51·8°, and 51·8° respectively. More solid was added between each determination, and since this addition caused no further alteration in the value after the third determination, the transition point may be taken as 51·8°.
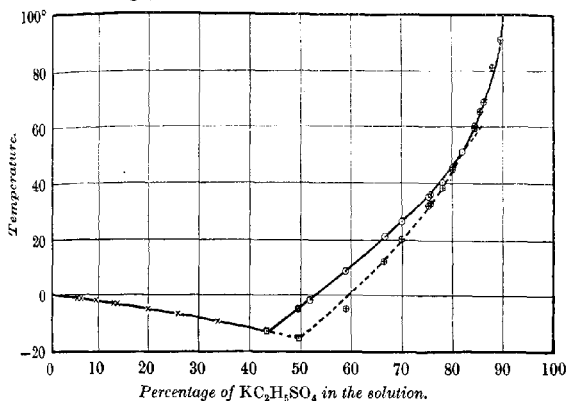
FIG. 2.

The System: Potassium Ethyl Sulphate–Water.
⊙ a-Form.   × Ice line.
⊕ β-Form.   ⊡ Eutectics.

Percentage of $KC_2H_5SO_4$ in the solution.

In order to complete the diagram representing the systems of potassium ethyl sulphate and water, the ice line was determined. The depressions of the freezing point of water by various amounts of the dissolved salt were found by the Beckmann method. The results are given in the following table :

Percentage of $KC_2H_5SO_4$ in the solution.	Freezing point.	Percentage of $KC_2H_5SO_4$ in the solution.	Freezing point.
5·480	−1·195°	13·770	−3·220°
6·370	−1·42	19·808	−4·93
9·434	−2·130	25·953	−6·68
12·953	−2·98	33·714	−9·55

The curve is plotted in Fig. 2, and agrees with that given by Illingworth and Howard (Phil. Mag., 1884, 18, 123).

The direct determination of the cryohydric points, both stable and metastable, was carried out by cooling a concentrated solution. After ice or potassium ethyl sulphate had ceased separating out alone, and the composition and temperature of the remaining

3 Q * 2

solution had attained those of the eutectic, subsequent solidification took place at constant temperature. This constant temperature was taken as the cryohydric point.

The values obtained for the α-eutectic point were $-12 \cdot 8°$ and $-13 \cdot 0°$. These agree with the extrapolated value, but not with that given by Illingworth and Howard.

The β-eutectic (metastable) was observed first at $-15 \cdot 1°$ to $-15 \cdot 3°$ and then at $-15 \cdot 2°$.

The mean values are therefore : for the α-eutectic $-12 \cdot 9°$, and for the β $-15 \cdot 2°$.

We conclude by expressing our gratitude to Brig.-Gen. H. B. Hartley for his valuable help and advice.

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CCVI.—The Friedel-Crafts' Reaction. Part III. Migration of Alkyl Groups in the Benzene Nucleus.

By MAURICE COPISAROW.

THE chemical metabolism brought about by the action of aluminium chloride on alkylated hydrocarbons of the aromatic series results in profound molecular rearrangements.

The scission of alkyl groups in the benzene series by means of aluminium chloride was first recorded by Gustavson (Bull. Soc. chim., 1878, [ii], **30**, 22), and by Friedel and Crafts (T., 1882, 41, 116).

Further work by Friedel and Crafts (T., 1885, **48**, 674), Anschutz and Immendorf (Ber., 1885, **18**, 657), and Heise and Tohl (Annalen, 1892, **270**, 168) indicated that the action of aluminium chloride results in a general migration of alkyl and, to a smaller extent, of phenyl groups, with the formation of isomerides, higher and lower alkyl derivatives of benzene, and members of the diphenyl group.

In the light of the investigations of Friedel and Crafts (Compt. rend., 1885, **100**, 692), Hamer (Proc. Camb. Phil. Soc., 1911, 16, 65), Schröeter (Brennstoff Chem., 1920, **1**, 39), Zanetti and Kinda (J. Ind. Eng. Chem., 1921, **13**, 208, 358), and Copisarow (this vol. p. 442) the action of aluminium chloride appears to extend beyond

the migration of groups and results in pyrogenic-like fission of the benzene nucleus with the formation of members of the naphthalene, anthracene, and probably phenanthrene series. The action of ferric chloride on alkyl derivatives of benzene results, not only in migration, but also in chlorination (Thomas, *Compt. rend.*, 1898, **126**, 1213).

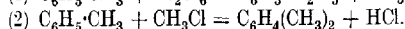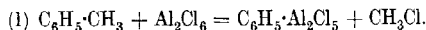In the course of the present investigation the following facts were established :

(1) The action of aluminium chloride on methylated benzene represents qualitatively a reversible reaction in so far as the migration of the alkyl groups is concerned, and, therefore, in this respect it lends itself to the same treatment as is applied in the migration of the halogen atoms (Copisarow, *loc. cit.*).

(2) The fission of the benzene nucleus is facilitated by high temperatures, concentration of aluminium chloride, extent of alkylation of the hydrocarbon, and extension of the period of reaction beyond the maximum required for the migration.

The optimum conditions for the migration were attained by modifying the conditions of reaction in the light of these observations, and also the observations made by Jacobson (*Ber.*, 1885, **18**, 338) and by Anschutz and Immendorf (*Annalen*, 1886, **235**, 177) on the influence of hydrogen chloride.

The increased migration is clearly illustrated by comparison of the 22·9 and 23·7 per cent. yields of toluene from xylene obtained in the present case with that of 12·5 per cent., the maximum found by Fischer and Niggemann (*Ber.*, 1916, **49**, 1475).

The rôle of hydrogen chloride in the reaction consists in its action on the double compound formed by the hydrocarbons with aluminium chloride. Its effect may be expressed by the equations :

(1) $C_6H_5 \cdot CH_3 + Al_2Cl_6 = C_6H_5 \cdot Al_2Cl_5 + CH_3Cl$.
(2) $C_6H_5 \cdot CH_3 + CH_3Cl = C_6H_4(CH_3)_2 + HCl$.
(3) $C_6H_5 \cdot Al_2Cl_5 + HCl = C_6H_6 + Al_2Cl_6$.

The influence of nitrogen is merely mechanical, whilst the chemical effect of hydrogen is probably due to its action on the methyl chloride formed in the course of the reaction.

The duration of heating was regulated in the experiments carried out in distillation apparatus by the rate of distillation of the products of low b. p.

The limitations of the progress of migration must be attributed to the deteriorating effect of the fission products upon the active surface of the aluminium chloride, rather than to the formation of the fission products as such.

EXPERIMENTAL.

[With CYRIL NORMAN HUGH LONG.]

The Action of Aluminium Chloride on Toluene.

Series I.—Mixtures of toluene (5 parts) and finely powdered aluminium chloride (1 part) were heated on the steam-bath for eight hours under reflux, in one case in presence of a current of nitrogen and in the other of hydrogen chloride at the approximate rate of 3 bubbles per second.

The mixtures gradually darkened with the formation of a deep-red double compound of aluminium chloride with the hydrocarbons present. The reaction mixtures were subsequently treated with ice and a little hydrochloric acid and distilled in a current of steam. The oily layer of the distillate was removed, dried over sodium sulphate, and fractionally distilled, the following fractions being collected : (*a*) up to 100°, (*b*) 100—125°, (*c*) 125—155°, and (*d*) above 155°. On carefully refractionating and comparing these distillates with known mixtures of benzene, toluene, and xylene fractionated in the same apparatus, the following results were obtained :

	In nitrogen.	In hydrogen chloride.
		Yield per cent. of the theoretical.
Benzene	8·0	11·5
Toluene	90·5	60·0
Xylene (b. p. 136—143°)	7·0	5·3

The calculation of yields was based on the equation :

$$2C_6H_5 \cdot CH_3 = C_6H_6 + C_6H_4(CH_3)_2.$$
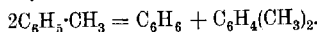
The fractions of high b. p. consist mainly of polyalkylbenzenes, whilst the small quantities of dark tarry residues left after distillation with steam represent the bulk of the products of fission.

In view of the work of Friedel and Crafts (*loc. cit.*), Anschutz and Immendorf (*loc. cit.*), and Copisarow (*loc. cit.*) no effort was made either to separate the polyalkylbenzenes, constituting the fraction of high b. p., or to isolate the complex mixture of hydrocarbons of the tarry residue.

Series II.—Mixtures of toluene and aluminium chloride, in proportions as above, contained in distillation flasks, were heated in presence of currents of nitrogen, hydrogen, and hydrogen chloride, the feature of these experiments being the removal of the products of low b. p., immediately they were formed, from the reaction media.

The temperature, duration of reaction, and method of working up were similar to those employed in series I.

The following results were obtained :

	Yield per cent.		
	In nitrogen.	In hydrogen.	In hydrogen chloride.
Benzene (before and after working up)	14·2	20·8	25·9
Toluene	63·0	77·0	57·8
Xylenes	5·7	8·0	6·5

The fractions of high b. p. and the tarry residue, especially the former, were very small in the experiment carried out in presence of hydrogen.

Series III.—A mixture of toluene (100 parts) and aluminium chloride (3 parts), contained in a distillation flask, was heated in presence of a current of hydrogen chloride, the experimental conditions being identical to those adopted in series II.

The following results were obtained :

Benzene	22·0 per cent. of the theoretical
Toluene	74·2 ,, ,, ,,
Xylenes	17·8 ,, ,, ,,

The quantity of other products was small.

The Action of Aluminium Chloride on Commercial Xylene.

The xylene employed in the subsequent experiments was prepared by washing crude commercial xylene with a little (6 per cent.) cold concentrated sulphuric acid, with sodium hydroxide, and with water, then drying over sodium sulphate and fractionally distilling, the fraction boiling at 136—143° being utilised.

Series I.—Mixtures of purified commercial xylene (5 parts) with finely powdered aluminium chloride (1 part), contained in a distillation flask, were heated for eight hours in presence of a current of hydrogen chloride.

Experiments were carried out at 100° and 120°. The features of the reaction were similar to those of toluene.

The product of reaction, after treatment with ice and hydrochloric acid, was deep green and showed distinct fluorescence.

The following results were obtained on fractionation of the distillate in a manner identical to that adopted in the previous experiments.

	Yield per cent.	
	At 100°.	At 120°.
Benzene (before and after steam distillation)	7·7	4·1
Toluene ,, ,, ,,	23·7	16·3
Xylenes (b. p. 136—143°)	45·8	37·0

calculated on the basis of the equations :

$$2C_6H_4(CH_3)_2 = C_6H_5 \cdot CH_3 + C_6H_3(CH_3)_3 \text{ and}$$
$$2C_6H_4(CH_3)_2 = C_6H_6 + C_6H_2(CH_3)_4$$
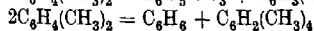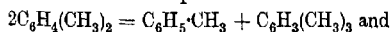
although some of the benzene formed may have been due to the action of aluminium chloride on the hydrocarbons produced during the reaction.   The residue left after steam-distillation was a viscous, dark-green tar.

Series II.—A mixture of xylene (100 parts) and aluminium chloride (3 parts) was heated at 120° under conditions identical to those of series I.

The product of reaction was pale green, and when subjected to distillation with steam, left but a small tarry residue.   The following results were obtained on fractionating the distillate :

Benzene .... 3·8 per cent. of the theoretical
Toluene .... 22·9   ,,   ,,   ,,
Xylenes .... 50·4   ,,   ,,   ,,

The complexity and relative quantities of the fractions of high b. p. and residues may be seen from the table given below, 212 grams (2 gram-mols.) of xylene being employed in each experiment.

| | Series I. | | Series II. |
Fraction.	At 100°.	At 120°.	At 120°.
143—162°	10·4 grams	9·8 grams	30·4 grams
162—185°	42·0 ,,	16·3 ,,	35·4 ,,
185—195°	4·8 ,,	4 ,,	2·6 ,,
195—270°	5·2 .,	4 ,,	3 ,,
Residue (tar)	20 ,,	78 ,,	4 ,,

CHEMICAL DEPARTMENT,
THE UNIVERSITY, MANCHESTER.   [*Received, August 27th,* 1921.]
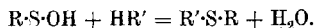

CCVII.—*Derivatives of* 3-*Oxy*(1)*thionaphthen.*

By SAMUEL SMILES and ERNEST WILSON MCCLELLAND.

THE experiments described in the following pages are the outcome of a previous investigation of the reactions of aromatic mercaptans in sulphuric acid solution.   In this medium oxidation of the mercaptan takes place, disulp̣ides being formed; the properties of the solution indicate that the disulphide is in equilibrium with the mercaptan and sulphenic acid :

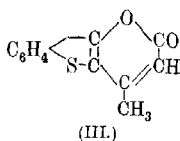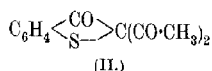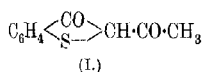$$R{\cdot}S{\cdot}S{\cdot}R \rightleftharpoons R{\cdot}S{\cdot}OH + R{\cdot}SH.$$

The presence of the sulphenic acid has been inferred from the reactions of these solutions.   By the addition of other compounds which contain hydrogen available for removal in the form of water, various types of sulphides have been isolated from them :

$$R'{\cdot}S{\cdot}OH + HR' = R'{\cdot}S{\cdot}R + H_2O.$$

In the case of 2-thiolbenzoic acid and the corresponding disulphide it has been shown that aromatic compounds yield the thioxanthones and that aliphatic compounds containing the ketomethylene group furnish derivatives of 3-oxy(1)thionaphthen; for example, malonic acid or ethyl acetoacetate (T., 1912, **101**, 572) yielded this substance :
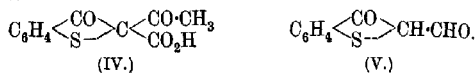
$$C_6H_4{<}^{S \cdot OH}_{CO_2H} + CH_2(COR)_2 = C_6H_4{<}^{S-}_{CO}{>}CH_2 + 2R \cdot CO_2H.$$
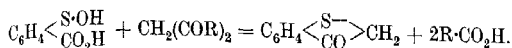
In simple cases such as these the groups $R \cdot CO \cdot$ were found to be eliminated during the condensation, in fact in only one case, that of benzoylacetone, from which 2-benzoyl-3-oxy(1)thionaphthen was obtained, did the product contain the ketonic group of the original substance. The study of this type of reaction was interrupted and a somewhat incomplete account of the results was published (Smiles and Ghosh, T., 1915, **107**, 1378). The experiments which are now described were carried out primarily with the object of obtaining further evidence that derivatives of 3-oxy(1)thionaphthen with substituents in position 2 are formed in the earlier stages of the reaction. This evidence has been obtained in two ways : either by employing milder conditions of reaction which permit these substitution products to escape decomposition, or by choosing material which furnishes characteristic derivatives of greater stability.

$$C_6H_4{<}^{CO}_{S-}{>}CH \cdot CO \cdot CH_3 \qquad\qquad C_6H_4{<}^{CO}_{S-}{>}C(CO \cdot CH_3)_2$$
$$\text{(I.)} \qquad\qquad\qquad\qquad \text{(II.)}$$

(III.)

In previous experiments with the condensation of 2-thiolbenzoic acid and acetylacetone the formation of 3-oxy(1)thionaphthen was recorded (Smiles and Ghosh, *loc. cit.*). By repeating the process at lower temperatures 2-acetyl-3-oxy(1)thionaphthen (I) has now been obtained in good yield, but the diacetyl derivative (II), which is no doubt the primary product, could not be isolated. In the case of ethyl acetoacetate it has been shown (T., 1912, **101**, 572; 1915, **107**, 1379) that with 2-thiolbenzoic acid and sulphuric acid at 90° "thioindigo," small amounts of oxythionaphthen, and the methylcoumarin (III) are formed. Further experiments carried out at lower temperatures have yielded none of these, but instead gave a product which from its general properties appears without

doubt to be the acid (IV). This substance proved too unstable for isolation in a state fit for analysis; oxythionaphthen, in place of the 2-acetyl derivative as expected, being formed from it by hydrolysis with alkaline or acid media or even by mere recrystallisation.
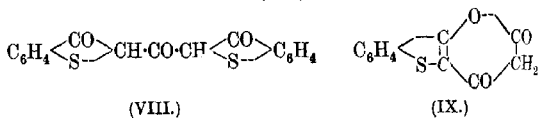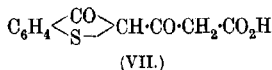
$$C_6H_4{<}{\overset{CO}{\underset{S}{}}}{>}C{<}{\overset{CO\cdot CH_3}{\underset{CO_2H}{}}} \qquad\qquad C_6H_4{<}{\overset{CO}{\underset{S}{}}}{>}CH\cdot CHO.$$

(IV.)   (V.)

According to the work of von Pechmann (*Ber.*, 1884, **17**, 932), the solution of malic acid in sulphuric acid may be used for generating malonic semialdehyde in the production of coumarins from phenols. This solution also undergoes reaction with 2-thiolbenzoic acid, yielding the 3-oxy(1)thionaphthen-2-aldehyde (V). The aldehyde acid would appear to be formed in the first stage of the process before loss of carbon dioxide takes place; but the amount

$$C_6H_4{<}{\overset{CO}{\underset{S}{}}}{>}CH\cdot CH{:}C{<}{\overset{CO}{\underset{S}{}}}{>}C_6H_4$$

(VI.)
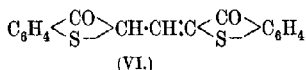
of the aldehyde met with is quite small, the chief product being the red dyestuff (VI) which is formed from it by the action of sulphuric acid (Friedländer, *Ber.*, 1911, **44**, 3100).
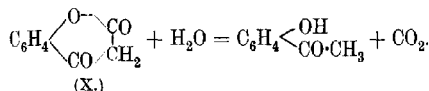
The reaction of 2-thiolbenzoic acid with acetonedicarboxylic acid or with citric acid in sulphuric acid solution has also been studied. The presence of two methylene groups in acetonedicarboxylic acid suggests the possibility that this might unite with one or two molecules of the mercaptan according to the proportions of the reagents present, yielding after loss of carbon dioxide the following substances (VII or VIII) :

$$C_6H_4{<}{\overset{CO}{\underset{S}{}}}{>}CH\cdot CO\cdot CH_2\cdot CO_2H$$

(VII.)

$$C_6H_4{<}{\overset{CO}{\underset{S}{}}}{>}CH\cdot CO\cdot CH{<}{\overset{CO}{\underset{S}{}}}{>}C_6H_4 \qquad\qquad C_6H_4{<}{\overset{-C}{\underset{S-C}{}}}{<}{\overset{O-}{\underset{CO}{}}}{<}{\overset{CO}{\underset{CH_2}{}}}$$

(VIII.)   (IX.)

3-Oxy(1)thionaphthen yields the methylcoumarin (III) on treatment with ethyl acetoacetate in presence of sulphuric acid and, bearing in mind the stability of this coumarin, it must be expected that if a product of type VII were formed, it should be converted by loss of water to the oxycoumarin (IX). This substance has been obtained from the reaction of acetonedicarboxylic acid with 2-thiolbenzoic acid, in fact it appears to be the sole product; a

substance derived from type VIII has not been isolated even when excess of the mercaptan was taken.

The structure assigned to this product has been proved by the isolation of the thionaphthen nucleus with the acetyl group derived from the oxycoumarin complex, and by the fact that the substance possesses the characteristic properties of benzotetronic acid (X), or 4-oxycoumarin, which it closely resembles. By distillation with a current of steam the compound yields, with loss of carbon dioxide and absorption of the elements of water, 2-acetyl-3-oxy(1)thionaph-'hen (I). The constitution of the latter substance is determined py (1) the synthesis from acetylacetone as described in a foregoing paragraph, (2) the conversion to "thioindigo" by alkaline ferri-cyanide, and (3) the formation of a phenylhydrazone. Moreover, the coumarin derivative is soluble in aqueous sodium carbonate solution; it yields a nitroso-derivative, and on treatment with formaldehyde furnishes the corresponding methylene-bisthionaphtha-oxycoumarin. These properties are in close accord with those assigned to benzotetronic acid by Anschutz (*Annalen*, 1909, **367**, 169; 1911, **379**, 333), who recorded the formation of the nitroso- and bismethylene derivatives and the hydrolysis by alkali hydroxide with formation of 2-hydroxyacetophenone :

$$C_6H_4 \diagdown \begin{matrix} O \cdots \diagdown CO \\ CO \diagup CH_2 \end{matrix} + H_2O = C_6H_4 \diagdown \begin{matrix} OH \\ CO \cdot CH_3 \end{matrix} + CO_2.$$
$$(X.)$$

From the experiments which have now been made on this subject, it is clear that the reaction between 2-thiolbenzoic acid and substances containing the ketomethylene group is of fairly wide application. In all the cases examined the formation of derivatives of 3-oxy(1)thionaphthen has been shown, and from the evidence collected there is little doubt that the 2-derivatives of this substance are the primary products, which, under certain conditions, such as high temperature, may suffer decomposition, yielding the parent oxythionaphthen.

EXPERIMENTAL.

1. *Ethyl Acetoacetate and 2-Thiolbenzoic Acid* (compare T., 1912, **101**, 572).—Twelve grams of ethyl acetoacetate were slowly added to a mixture of 10 grams of 2-thiolbenzoic acid and 120 grams of concentrated sulphuric acid. The solution was continually shaken during the addition of the ester, and the temperature was maintained at 28—30°. The reaction progressed with evolution of sulphur dioxide and solution of the dithiobenzoic acid; it was complete in

about thirty-five minutes. The mixture was then poured over crushed ice and the yellow solid was collected and washed with water. The filtrate contained a small quantity of oxythionaphthen. The solid material proved to be very unstable, being easily resolved into oxythionaphthen; it was obtained in the crystalline state, but still impure, by the slow addition of water to the solution in alcohol. It is soluble in aqueous sodium carbonate, and when heated it decomposes rapidly with effervescence. When treated with a current of steam in presence of a little dilute sulphuric acid, the substance yielded 2-oxy(1)thionaphthen and a considerable quantity of " thioindigo." From 10 grams of thiolbenzoic acid 5 grams of oxythionaphthen were isolated. Hydrolysis may also be effected by dilute aqueous ammonia. The methylcoumarin isolated in previous experiments was not observed in the product formed under these conditions.

2. *2-Acetyl-3-oxy(1)thionaphthen* (formula I).—This substance was prepared from the thionaphthacoumarin derivative described in a subsequent paragraph, and by the action of acetylacetone on 2-thiolbenzoic acid.

(a) The crude thionaphthoxycoumarin obtained from the interaction of citric acid and 2-thiolbenzoic acid was treated with a current of steam in presence of a little dilute sulphuric acid. The first portion of the distillate contained oxythionaphthen which had been formed during the preparation of the coumarin derivative by the action of hot concentrated sulphuric acid on that substance. The solid which separated from the subsequent distillate was collected and recrystallised from aqueous alcohol; 2-acetyl-3-oxy(1)thionaphthen was thus obtained in pale yellow needles which melted at 81°. The substance is very soluble in most organic media and sparingly so in water (Found : C = 62·1 ; H = 4·2; S=16·9 ; $M = 186$. $C_{10}H_8O_2S$ requires C = 62·45 ; H = 4·19; S = 16·69 per cent.; $M = 192$). The addition of ferric chloride to the alcoholic solution produces a green colour. With hot concentrated sulphuric acid " thioindigo " is slowly formed and the same substance is readily obtained by the addition of potassium ferricyanide to the alkaline solution.

The *phenylhydrazone* of 2-acetyl-3-oxy(1)thionaphthen was prepared by boiling an alcoholic solution of the components for three hours. The crude product was recrystallised by the addition of water to the alcoholic solution ; the pure substance formed slender, reddish-brown needles which melted at 131° (Found : N = 10·0. $C_{16}H_{14}ON_2S$ requires N = 9·9 per cent.). The scarlet sodium salt of this hydrazone is sparingly soluble in water.

(b) Five grams of 2-thiolbenzoic acid were suspended in 50 c.c.

of concentrated sulphuric acid; 3·3 grams of acetylacetone were then gradually added to the mixture, which was kept at 40° for three-quarters of an hour. The solid material obtained by pouring this mixture over crushed ice was washed with water and then treated with a current of steam. The volatile product, after recrystallisation from aqueous alcohol, was identical with that obtained in the foregoing preparation; samples of the phenyl-hydrazone prepared from the two sources also were identical.

3. *3-Oxy*(1)*thionaphthen-2-aldehyde* (formula V).—A mixture of 10 grams of 2-thiolbenzoic acid and 100 c.c. of concentrated sulphuric acid was heated rapidly to 90°; 15 grams of finely powdered malic acid were then added in the course of fifteen minutes, the contents of the vessel being constantly shaken. After remaining at 90° for another period of fifteen minutes, the mixture was rapidly cooled and then poured over ice. The solid material was collected and thoroughly washed with water; then the aqueous filtrates were shaken with ether, and the solid remaining after this solvent had been evaporated was treated with a current of steam. After recrystallisation, the volatile product melted at 107° (Found : $S = 18·1$. Calc., $S = 18·0$ per cent.). It reduced an ammoniacal solution of silver oxide, imparted a green colour to an alcoholic solution of ferric chloride, and with dilute sulphuric acid readily yielded the red dyestuff (formula VI). In all these properties the substance entirely agrees with the 3-oxy(1)thionaphthen-2-aldehyde previously prepared by Friedländer (*loc. cit.*) from " 2-thionaphthen-3-indole-indigotin " (3'-indoxyl-2-thionaphthen-3-one) with sodium ethoxide. The phenylhydrazone was prepared (Found : $N = 10·4$. Calc., $N = 10·4$ per cent.), it melted at 136—137°; Friedländer gives 137° as the melting point of this substance. The yields of the aldehyde in this process are very poor, but this is not surprising, since in presence of mineral acids it is readily converted (Friedländer, *loc. cit.*) to the red condensation product. This substance forms the chief product of the reaction now described; it was obtained from the solid material by extraction with a hot dilute solution of sodium hydroxide.

4. (1)*Thionaphtha-4-oxycoumarin* (formula IX).—A mixture of 5 grams of 2-thiolbenzoic acid and 12 grams of acetonedicarboxylic acid was added to 50 c.c. of concentrated sulphuric acid. The reaction which set in immediately was completed by keeping the solution at 40—50° for one and a half hours. When the evolution of sulphur dioxide had ceased, the mixture was poured over ice, and the precipitated solid was collected and washed until free from acid. It was then recrystallised from aqueous alcohol, when (1)thionaphtha-4-oxycoumarin was obtained in faintly yellow

needles which melted and decomposed at about 275° (Found:
C = 60·1; H = 2·9; S = 14·7. $C_{11}H_8O_3S$ requires C = 60·51;
H = 2·77; S = 14·7 per cent.). The substance is insoluble in
water and soluble in aqueous sodium hydroxide or carbonate.
The action of sodium nitrite yields a yellow nitroso-derivative.
The same material is readily prepared by substituting 15 grams of
citric acid for the acetonedicarboxylic acid mentioned in the fore-
going preparation; at the same time the amount of sulphuric
acid should be increased to 80 c.c., but the temperature quoted
should not be exceeded, otherwise oxythionaphthen is formed by
decomposition of the coumarin derivative. The formation of
2-acetyl-3-oxy(1)thionaphthen from this substance by treatment
with steam is described in a foregoing paragraph.

Methylene bis-(1)thionaphtha-4-oxycoumarin was prepared by the
action of formaldehyde upon this coumarin derivative. The
substance was easily obtained in the pure condition by adding the
calculated quantity of 40 per cent. aqueous formaldehyde to a
solution of the naphthacoumarin in alcohol. The mixture was
then set aside in a stoppered flask, when the desired substance
was gradually precipitated in the crystalline state. The material
was collected and the adherent components were removed by
boiling alcohol (Found: C = 61·3; H = 3·0; S = 14·3. $C_{23}H_{12}O_6S_2$
requires C = 61·57; H = 2·69; S = 14·3 per cent.). The sub-
stance is insoluble in water and most organic media; it dissolves
in hot nitrobenzene, from which it separates in small, yellow needles;
these melt and decompose at about 300°.

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CCVIII.—*A New Method for the Resolution of Asymmetric Compounds.*

By AKIRA SHIMOMURA and JULIUS BEREND COHEN.

THE production of optically active substances in the living organism
is attributed in certain cases to their synthesis in association with
active protein or other active constituent of the body. If this is
the case, a substance which is already asymmetric in structure
would probably yield an active product, that is, a preponderance of
one of the active constituents of the mixture, if the asymmetric

roup were to undergo substitution in combination with active material. Such a process would represent, in the usual acceptation f the term, a modified form of asymmetric synthesis; but as the riginal molecule, although inactive, has an asymmetric structure, e prefer to call it a new method for the resolution of asymmetric mpounds. Thus, supposing an inactive mixture $C(abcd)$ be mbined with an active group, and under such asymmetric conitions d be replaced by e, yielding $C(abce)$, then, according to the bove principle, the latter compound, when separated from the tive group, should exhibit, in a greater or less degree, optical tivity.
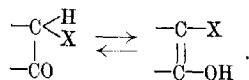
It was with the object of testing the accuracy of this principle lat the present research was initiated. The choice of a simple mbination between an asymmetric group and an active substance ppeared to be limited to the esters of an asymmetric acid with active alcohol, or to an amide of a similar acid with an active nine. In the first instance, preference was given to the amide mbination, as such substances can, as a rule, be hydrolysed by ids without racemisation, whereas hydrolysis of an ester by kalis may produce inactivity unless great care is exercised. A rious observation was made in the case of certain amides of enthylamine and bornylamine, which were so stable as to resist ll attempts at hydrolysis by acids.

The following typical series of substitutions were examined :

$$\text{Cl,Br} \xrightarrow{\text{NH}_4} \text{NH}_2 ; \ \text{Cl,Br} \xrightarrow{\text{M'OH}} \text{OH} ; \ \text{OH} \xrightarrow[\text{PCl}_5]{\text{SOCl}_2} \text{Cl} ; \ \text{NH}_2 \xrightarrow{\text{HNO}_2} \text{OH}.$$

$$\text{(I.)} \qquad\qquad \text{(II.)} \qquad\qquad \text{(III.)} \qquad\quad \text{(IV.)}$$
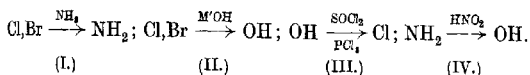
The results showed that in the case of I and II, either racemisaion occurred or the substance was unchanged, but both III and IV ielded active products.

It is possible that in the first two cases, in which acid radicles ontaining the group $-\text{CHX}\cdot\text{CO}-$ $(X = \text{Cl,Br})$ were employed, form of tautomerism might take place, causing racemisation hus :

$$\begin{array}{c} -\text{C} <_{\text{X}}^{\text{H}} \\ | \\ -\text{CO} \end{array} \ \underset{\longleftarrow}{\overset{\longrightarrow}{}} \ \begin{array}{c} -\text{C}-\text{X} \\ || \\ -\text{C}-\text{OH} \end{array} .$$

We therefore propose to repeat these experiments, using compounds in which hydrogen is not attached to the asymmetric arbon.

The following is a summary of the results : The action of ammonia r water with the addition of silver oxide or sodium carbonate on

l-menthyl dl-phenylchloroacetate, and of ammonia on l-menthyl dl-phenylbromoacetate and l-menthyl dl-α-bromo-β-phenylpropionate gave negative results. A similar result was obtained when ammonia was allowed to react with α-bromopropionyl-l-tyrosine. Neither phenylchloroaceto-d-bornylamide nor the l-menthylamide was found suitable for conversion into the amino-compounds.

By the action of thionyl chloride and phosphorus pentachloride on l-menthyl dl-mandelate and subsequent removal of menthol, active phenylchloroacetic acid was obtained, the product in the first case giving a rotation of $[\alpha]_{b}^{15^{\circ}} - 10°$, and in the second $[\alpha]_{b}$ $- 8·1°$.

When dl-phenylchloroacetyl-l-tyrosine was heated with strong ammonia, and the amino-compound treated with nitrous acid and finally the l-tyrosine removed, the mandelic acid, thus obtained, showed a rotation of $[\alpha]^{9°} + 11·5°$ in alcoholic solution.

Although the number of positive results are few, they are sufficient to establish the accuracy of the principle, which we hope to extend in a subsequent paper.

EXPERIMENTAL.

Preparation of 1-Menthyl dl-Phenylchloroacetate,
$$C_6H_5 \cdot CHCl \cdot CO_2 \cdot C_{10}H_{19}.$$
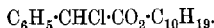
A molecular mixture of l-menthol and dl-phenylchloroacetyl chloride was heated at 110° for two and a half hours and then at 150° for one hour. The product was extracted with ether. After the ethereal extract had been washed with water and a dilute solution of sodium carbonate, it was dried over sodium sulphate and the ether driven off. The remaining oil was fractionated under diminished pressure and the portion which distilled at 222°/25 mm. (or 220°/22 mm., 210°/18 mm.) collected; 82 per cent. of the theoretical yield was obtained in a favourable case (Found : Cl = 11·66. $C_{18}H_{25}O_2Cl$ requires Cl = 11·49 per cent.). l-Menthyl dl-phenylchloroacetate, when freshly distilled, is an almost colourless, strongly refracting, viscous oil, having d_{22}^{23} 1·070 and $[\alpha]_{b}^{15} - 68·55°$ ($\alpha = - 22·15°$, $l = 0·302$).

The oil subsequently solidified to a crystalline mass, melting at 30—41°, after having been kept at the ordinary temperature for eight days. It was easily soluble in alcohol, ether, or light petroleum, but insoluble in water.

Partial resolution of the compound into diastereoisomerides by fractional crystallisation seems to be possible (Wren and Wright, this vol., p. 798). By repeated recrystallisation from alcohol, an

ester, having m. p. 34—40° and $[\alpha]_{D}^{15°}$ — 92·25° ($c = 2$, $l = 2$) in alcoholic solution, was obtained, which on hydrolysis gave a slightly lævorotatory phenylchloroacetic acid.

An attempt to replace the halogen atom of menthyl phenylchloroacetate by the hydroxyl group by the action of cold or hot water, silver oxide, or sodium carbonate was unsuccessful owing to the great stability of the ester towards these agents.

Action of Ammonia on 1-Menthyl dl-Phenylchloroacetate.

Ordinary concentrated ammonia has little action on the compound either at the ordinary temperature or at 100°. The replacement of the chlorine atom by the amino-group was effected to some extent by dissolving the compound in concentrated alcoholic ammonia and maintaining the mixture first at the ordinary temperature for several days and then at 90—100° for about three hours. By the above treatment, in addition to the amino-ester which was formed, a small quantity of the ester was hydrolysed at the same time, menthol being eliminated.

Four grams of l-menthyl dl-phenylchloroacetate (b. p. 222°/ 25 mm.) and 50 c.c. of concentrated alcoholic ammonia were placed in a tube, which was then sealed and kept at the ordinary temperature for two days and finally heated at 90—100° for about three hours. The product was carefully evaporated on the waterbath, the residue shaken with ether, dilute hydrochloric acid added, and the mixture again well shaken, whereby the hydrochloride of menthyl phenylaminoacetate was thrown down as a white, flocculent precipitate, which was almost insoluble in cold, but fairly soluble in hot water, from which it crystallised in fine, colourless needles, melting and decomposing at 249°.

The free amino-ester was obtained by adding ammonia to the hot aqueous solution of the hydrochloride and extracting the separated oil with ether. After being kept over-night in an icechest, it solidified gradually to a crystalline mass, which, when pressed on a porous plate and recrystallised from alcohol, was obtained in silky needles of m. p. 55° (Found: $N = 5·09$. $C_{18}H_{27}O_2N$ requires $N = 4·84$ per cent.). It was soluble in the ordinary organic solvents and showed $[\alpha]_{D}^{16}$ — 147·3° ($c = 0·930$, $l = 2$) in alcoholic solution.

Menthyl phenylaminoacetate (m. p. 54—55°) could also be obtained directly, in a very poor yield, by passing, from time to time, dry hydrogen chloride through a molten mass of phenylaminoacetic acid in an excess of menthol, which was heated on a water-bath for about eight hours.

In order to hydrolyse menthyl phenylaminoacetate, the compound was dissolved in a slight excess of alcoholic potassium hydroxide (1 c.c. contains 0·016 gram of potassium hydroxide) and kept at the ordinary temperature for five days. The alcohol was evaporated at the ordinary temperature and the residue extracted with warm dilute hydrochloric acid. The filtered acid solution was extracted with ether and then distilled with steam in order to remove any trace of menthol. It was then made slightly alkaline with ammonia, whereby phenylaminoacetic acid was precipitated, which was thoroughly washed with ether to remove any unchanged amino-ester. The phenylaminoacetic acid, thus recovered, melted toward 266°, subliming mostly below that temperature, and showed no appreciable optical activity in dilute hydrochloric acid.

Preparation of l-Menthyl dl-Phenylbromoacetate, $C_6H_5 \cdot CHBr \cdot CO_2 \cdot C_{10}H_{19}$.

A molecular mixture of l-menthol and dl-phenylbromoacetyl bromide was heated at 100—110° for two hours and then at 150° for half an hour. The product was purified as in the case of the chlorine compound. The oil, which distilled at 220—225°/20 mm., solidified to a crystalline mass when kept over-night in the ice-chest. The yield was about 50 per cent. of the theoretical. By repeated recrystallisation from alcohol, the ester was obtained in colourless needles of m. p. 84°, showing $[\alpha]_D^{16°} + 2 \cdot 2°$ ($c = 0·68$, $l = 2$) in alcoholic solution (Found : Br = 22·34. $C_{18}H_{25}O_2Br$ requires Br = 22·63 per cent.). The small dextrorotation of the recrystallised product is probably due to partial resolution of the acid radicle. The ester, on hydrolysis, gave a menthol showing $[\alpha]_D^{18°}$ about − 57° in alcoholic solution.

Action of Ammonia on l-Menthyl dl-Phenylbromoacetate.

Two grams of the bromine compound (b. p. 220—225°/20 mm.) were dissolved in 25 c.c. of concentrated alcoholic ammonia and kept at the ordinary temperature for sixteen days and then finally heated at 80—90° for three hours. The hydrochloride of menthyl phenylaminoacetate (Found : Cl = 11·3. $C_{18}H_{28}O_2NCl$ requires Cl = 10·9 per cent.) melted and decomposed at 245°. The free amino-ester melted at about 55°.

The phenylaminoacetic acid, recovered by hydrolysing the ester with alcoholic potassium hydroxide, was quite inactive in dilute hydrochloric acid.

Preparation of l-*Menthyl* dl-*α-Bromo-β-phenylpropionate,*
$$C_6H_5 \cdot CH_2 \cdot CHBr \cdot CO_2 \cdot C_{10}H_{19}.$$

A molecular mixture of *dl*-α-bromo-β-phenylpropionyl chloride and *l*-menthol was heated at 100° for two and a half hours and then at 150° for half an hour. The portion which distilled at 212°/15 mm. was collected. The yield was about 76 per cent. of the theoretical. When the oil was kept at the ordinary temperature for a week, it began to solidify in colourless prisms melting at 46—51°. It was obtained in colourless needles of m. p. 50—51° by recrystallisation from alcohol (Found : Br = 21·79. $C_{19}H_{27}O_2Br$ requires Br = 21·76 per cent.). It showed $[\alpha]_D^{\circ} - 43\cdot8°$ $(c = 2, l = 2)$ in alcoholic solution.

This compound seems to undergo partial resolution by fractional crystallisation from alcohol, for the compound after crystallisation gave a slightly lævorotatory acid on hydrolysis, whilst that before crystallisation gave an inactive acid by the same treatment.

The compound was acted on by concentrated alcoholic ammonia, the mixture being kept at the ordinary temperature for seven days, and the product was subsequently hydrolysed in the usual way. The amino-acid recovered showed no appreciable activity.

Action of Thionyl Chloride on l-*Menthyl* dl-*Mandelate.*

l-Menthyl *dl*-mandelate was prepared according to the method of McKenzie (T., 1904, **85**, 383). The compound, unlike some compounds of other esters of a similar type, did not undergo any partial resolution by repeated recrystallisation (McKenzie, *loc. cit.*), for the mandelic acid recovered by hydrolysis was quite inactive.

Three grams of *l*-menthyl *dl*-mandelate and 8 grams of thionyl chloride were heated under reflux on a water-bath for two hours. After the excess of the thionyl chloride had been expelled under diminished pressure, the residue was extracted with ether, and the ethereal extract was washed with a dilute solution of sodium carbonate and dried over sodium sulphate. By evaporating the ether, a pale yellow oil was obtained.

In order to hydrolyse the product of chlorination, it was kept at the ordinary temperature for seven days with a slight excess of alcoholic potassium hydroxide. After the alcohol had been evaporated at the ordinary temperature, the residue was made distinctly alkaline with sodium carbonate solution and filtered from some solid matter (chiefly menthol), and any unchanged ester or residual menthol was removed by extraction with ether. The solution was then made acid with hydrochloric acid, whereby

phenylchloroacetic acid separated in an oily state. The whole was evaporated down on the water-bath to drive off any trace of menthol. The phenylchloroacetic acid, after being extracted with ether, showed in alcoholic solution $[\alpha]_0^{18°} - 10°$ ($c = 4.65, l = 2$).

Action of Phosphorus Pentachloride on l-Menthyl dl-Mandelate.

Five grams of l-menthyl dl-mandelate and 10 grams of phosphorus pentachloride were heated on the water-bath for five hours and then at 135—140° for one hour. The phosphoryl chloride formed was decomposed by the addition of ice, and the whole was extracted with ether. The ethereal solution, after being dried, gave a certain amount of pale yellow oil. The product of chlorination was hydrolysed as described above, and the phenylchloroacetic acid recovered showed in alcoholic solution $[\alpha]_0^{18}$ $-8.1°$ ($c = 3.274, l = 2$).

Certain bornylamine and menthylamine derivatives of halogenated acids containing an asymmetric carbon atom were prepared, but owing to their striking stability towards hydrolysing agents and to the difficulty in the preparation of their corresponding amino-derivatives, these compounds were found unsuitable for our purpose.

α-Bromopropiono-d-bornylamide, $C_{10}H_{17} \cdot NH \cdot CO \cdot CHBr \cdot CH_3$.

Three grams of d-bornylamine hydrochloride were dissolved in 30 c.c. of chloroform and the free base was liberated by the addition of 16 c.c. of N-sodium hydroxide. One half of a solution containing 4 grams of α-bromopropionyl bromide in 20 c.c. of chloroform was added to the cold solution of bornylamine, and the mixture was well shaken, the temperature being kept below 0° throughout the reaction. The remaining half of the acid bromide solution was then added, the reaction being kept always slightly alkaline by the occasional addition of sodium carbonate solution. When the reaction was complete, the chloroform layer was separated, and after being dried over sodium sulphate was evaporated as far as possible, and crude α-bromopropiono-d-bornylamide was precipitated by the addition of light petroleum. After repeated recrystallisation from dilute alcohol, it was obtained in fine, colourless needles, m. p. 144°, $[\alpha]_0^{15}$ $- 29.5°$ ($c = 1, l = 2$) in alcoholic solution (Found : Br $= 28.06$. $C_{13}H_{22}ONBr$ requires Br $= 27.73$ per cent.). It was soluble in alcohol, ether, chloroform, or acetone, difficultly soluble in boiling water, but insoluble in cold water or light petroleum.

Phenylchloroaceto-d-*bornylamide*, $C_{10}H_{17}\cdot NH\cdot CO\cdot CHCl\cdot C_6H_5$.

This amide was prepared in the same way as the above compound.
By repeated recrystallisation from alcohol, two compounds, one having m. p. 193° and the other m. p. 135°, were obtained. The former showed $[\alpha]_D^{16°} - 57\cdot0°$ $(c = 1, l = 2)$ in alcoholic solution (Found : Cl = 11·42. $C_{18}H_{24}ONCl$ requires Cl = 11·60 per cent.), whilst the latter showed $[\alpha]_D^{16°} + 2°$ $(c = 1, l = 2)$ in the same solvent (Found : Cl = 11·80. $C_{18}H_{24}ONCl$ requires Cl = 11·60 per cent.).

Phenylchloroaceto-l-*menthylamide*, $C_{10}H_{19}\cdot NH\cdot CO\cdot CHCl\cdot C_6H_5$.

In this case also two compounds were obtained, one having m. p. 174—175° and the other m. p. 113°, by repeated recrystallisation from alcohol. The former showed $[\alpha]_D^{16°} - 113°$ $(c = 0\cdot5, l = 2)$ in alcoholic solution (Found : Cl = 11·39. $C_{18}H_{26}ONCl$ requires Cl = 11·52 per cent.), whilst the latter showed $[\alpha]_D^{16°} - 47°$ $(c = 0\cdot5, l = 2)$ in the same solvent (Found : Cl = 11·44. $C_{18}H_{26}ONCl$ requires Cl = 11·52 per cent.).

The existence of two isomerides of the bornylamine and menthylamine derivatives is probably due to resolution of the acid radicle, but as the amides resisted hydrolysis by acids, the point could not be ascertained.

Preparation of dl-α-*Bromopropionyl*-l-*tyrosine*,
$OH\cdot C_6H_4\cdot CH_2\cdot CH(CO_2H)\cdot NH\cdot CO\cdot CHBr\cdot CH_3$.

Following Fischer's method for preparing chloroacetyl-*l*-tyrosine (*Ber.*, 1904, **37**, 2486), a satisfactory yield of α-bromopropionyl-*l*-tyrosine ethyl ester was obtained by treating *l*-tyrosine ethyl ester hydrochloride, having $[\alpha]_D^{18°} - 8\cdot3°$ $(c = 2, l = 2)$ in aqueous solution, with α-bromopropionyl bromide in an alkaline medium at a temperature below 0°, using chloroform as a solvent.

α-*Bromopropionyl*-l-*tyrosine ethyl ester* melted towards 131°, after having been twice precipitated from chloroform solution by the addition of light petroleum (Found : Br = 23·46. $C_{14}H_{18}O_4NBr$ requires Br = 23·22 per cent.). It was almost insoluble in cold water, with difficulty in hot water; soluble in alcohol, ether, or chloroform, but insoluble in light petroleum. It gave Millon's reaction and showed $[\alpha]_D^{15°} + 12\cdot5°$ $(c = 2, l = 2)$ in alcoholic solution.

Free α-bromopropionyl-*l*-tyrosine was obtained in an oily state by hydrolysing the ethyl ester with a dilute solution of sodium hydroxide at the ordinary temperature, and was found to be

identical with that which was prepared directly by the action of α-bromopropionyl bromide on *l*-tyrosine. The compounds obtained by both methods have much higher dextrorotatory power than the ethyl ester showing specific rotation between 30° and 40°.

Action of Ammonia on dl-α-Bromopropionyl-l-tyrosine.

Three grams of α-bromopropionyl-*l*-tyrosine were dissolved in 20 c.c. of concentrated aqueous ammonia and heated in a sealed tube in a water-bath for five hours. When the contents were evaporated, a syrupy mass was obtained, which, without further purification, was directly hydrolysed by boiling with concentrated hydrochloric acid. After the tyrosine had been removed, the solution, which should contain alanine, was examined polarimetrically, but showed no appreciable activity.

Preparation of dl-Phenylchloroacetyl-l-tyrosine,
$$OH \cdot C_6H_4 \cdot CH_2 \cdot CH(CO_2H) \cdot NH \cdot CO \cdot CHCl \cdot C_6H_5.$$
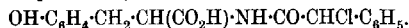
The direct synthesis of phenylchloroacetyl-*l*-tyrosine by the action of phenylchloroacetyl chloride on *l*-tyrosine was not successful. Its ethyl ester was therefore prepared in the same way as given above, and by subsequent hydrolysis, the free acid was obtained.

Phenylchloroacetyl-*l*-tyrosine ethyl ester was prepared in a moderate yield, in colourless needles (from alcohol) melting at 140—141° (Found : Cl = 9·87. $C_{19}H_{20}O_4NCl$ requires Cl = 9·80 per cent.). It gave Millon's reaction and showed $[\alpha]_D^{18°} +24°$ $(c = 1·5, l = 2)$ in alcoholic solution. It was almost insoluble in hot or cold water or light petroleum, but soluble in the other ordinary organic solvents.

Free phenylchloroacetyl-*l*-tyrosine was obtained by hydrolysing the ethyl ester with a dilute solution of sodium hydroxide at the ordinary temperature. It was obtained in small needles, melting towards 125° (Found : Cl = 10·20. $C_{17}H_{16}O_4NCl$ requires Cl = 10·63 per cent.).

It was moderately soluble in hot water, from which it separated in an amorphous state on cooling. It gave Millon's reaction.

Action of Ammonia on dl-Phenylchloroacetyl-l-tyrosine.

Two grams of the substance were dissolved in 20 c.c. of strong aqueous ammonia and warmed in a sealed tube at 80—90° for three hours. The product of amination, when carefully evaporated, gave a syrupy mass, which was used for the next experiment without further purification.

Action of Nitrous Acid on Phenylaminoacetyl-l-tyrosine.

The substance was dissolved in dilute hydrochloric acid and cooled to 0°, and the calculated quantity of sodium nitrite was then added and the mixture well stirred. The reaction was completed by warming on the water-bath for some time.

The product was then mixed with concentrated hydrochloric acid and boiled for two and a half hours under reflux in order to hydrolyse·it completely. After the intensely coloured solution had been treated with animal charcoal, it was neutralised with ammonia, whereby tyrosine was precipitated in white, microneedles, showing in $1.22N$-hydrochloric acid $[\alpha]_D^{19°} - 8.2°$ ($c = 0.669$, $l = 2$).

The filtrate was made distinctly acid by the addition of hydrochloric acid and extracted with ether. The ethereal solution, showing a slight dextrorotatory power, after having been dried over sodium sulphate, was shaken with a dilute solution of sodium hydroxide. The aqueous alkaline solution was again made acid by the addition of hydrochloric acid and finally extracted with ether. The dried ethereal extract, on evaporation, gave a small quantity of mandelic acid (melting towards 110°), which showed $[\alpha]_D^{19°} + 11.5°$ ($c = 0.13$, $l = 2$) in alcoholic solution.

THE ORGANIC CHEMICAL LABORATORIES,
THE UNIVERSITY, LEEDS.   [*Received, September 16th,* 1921.]

CCIX.—*Derivatives of Tetrahydrocarbazole.*

By WILLIAM HENRY PERKIN, jun., and SYDNEY GLENN PRESTON
PLANT.

INTEREST attaches to the reduction products of carbazole and particularly to tetrahydrocarbazole (I), in the first place because it is probable that strychnine is a derivative of the latter substance (compare Perkin and Robinson, T., 1910, **97**, 315), and secondly because tetrahydrocarbazole is structurally somewhat closely related to tetrahydroharmine (II) (T., 1919, **115**, 938).

(I.)   (II.)   (III.)
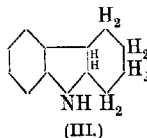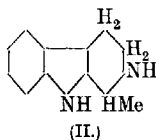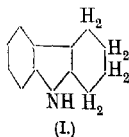
The reduction of carbazole, $C_{12}H_9N$, was first investigated by Graebe and Glaser (*Annalen*, 1872, **163**, 352), who showed that, when heated with hydriodic acid and phosphorus at 220—240°, it attaches six atoms of hydrogen yielding *carbazoline*, $C_{12}H_{15}N$, which is now known to have the constitution (III).

These investigators also showed that carbazoline hydrochloride is decomposed on distillation into hydrogen, hydrogen chloride, and tetrahydrocarbazole (m. p. 120°) :

$$C_{12}H_{15}N,HCl = H_2 + HCl + C_{12}H_{13}N.$$
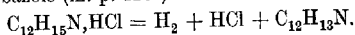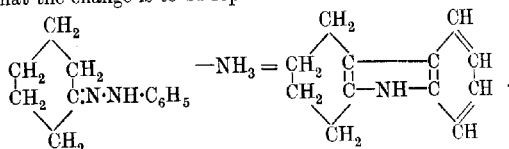
In 1888, Drechsel (*J. pr. Chem.*, 1888, [ii], **38**, 65) submitted phenol to electrolysis with an alternating current and isolated a substance, $C_6H_{10}O$ (b. p. 153—178°), which he named *hydropheno-ketone*. Drechsel combined this substance with phenylhydrazine and treated the product with dilute sulphuric acid, when he obtained a substance, $C_{12}H_{13}N$ (m. p. 108°), which he named *hydrophenanilide*. He recognised the fact that this substance had the same composition as Graebe and Glaser's tetrahydrocarbazole, but concluded that the substances were not identical because of the difference in their melting points.

Baeyer (*Ber.*, 1889, **22**, 2185; *Annalen*, 1894, **278**, 105) was the first to point out that Drechsel's hydrophenoketone is identical with *cyclo*hexanone and that hydrophenanilide, in spite of its rather low melting point, is tetrahydrocarbazole. He also pointed out that the conversion of the phenylhydrazone of *cyclo*hexanone into tetrahydrocarbazole is an example of the Fischer indole synthesis and that the change is to be represented thus :

$$\begin{array}{ccc}
CH_2 & CH_2 & CH \\
\end{array}$$

$$\begin{array}{l}
CH_2 \quad CH_2 \\
CH_2 \quad C{:}N{\cdot}NH{\cdot}C_6H_5 \\
CH_2
\end{array}
\;-NH_3 =
\begin{array}{l}
CH_2 \quad C \\
CH_2 \quad C{-}NH{-}C \\
CH_2
\end{array}
\quad
\begin{array}{l}
C \quad CH \\
CH \quad CH \\
CH
\end{array}$$

It is somewhat remarkable that this interesting substance has been so little investigated ; almost all that is known about its derivatives is due to the work of Borsche, Witte, and Bothe (*Annalen*, 1908, **359**, 53). These investigators were unsuccessful in their attempts to nitrate tetrahydrocarbazole (*loc. cit.*, p. 60) and prepared 8-nitro- and 6-nitro-tetrahydrocarbazoles,* m. p. 149° and 174° respectively

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* The scheme of numbering the positions in tetrahydrocarbazole employed in this communication is
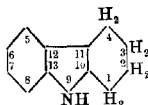
from the condensation products of *cyclo*hexanone with *o*- and *p*-nitrophenylhydrazine. In the case of the condensation product of *m*-nitrophenylhydrazine with *cyclo*hexanone they assume that the nitrotetrahydrocarbazole (m. p. 154°) produced by the action of dilute sulphuric acid is the 7-nitro-derivative, although it might well be the 5-nitro-derivative. This question of constitution is discussed in detail below.

The work described in the present communication may be briefly summarised as follows. We find, in the first place, that the phenylhydrazone of *cyclo*hexanone is converted almost quantitatively into tetrahydrocarbazole simply by boiling with glacial acetic acid, and in this and other similar cases the product is much cleaner than that obtained by the usual process, namely, boiling the phenylhydrazones with dilute sulphuric acid. The 9-acetyl derivative of tetrahydrocarbazole (IV, m. p. 78°), is readily obtained either by boiling *cyclo*hexanoneacetylphenylhydrazone with dilute sulphuric acid,

(IV.)
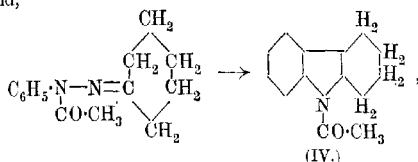
or directly from tetrahydrocarbazole by boiling with acetic anhydride or with acetyl chloride in the presence of copper powder at the ordinary temperature.

Contrary to the experience of Borsche, Witte, and Bothe (*loc. cit.*, p. 60), we find that it is possible to nitrate tetrahydrocarbazole direct if the solution in sulphuric acid is treated with potassium nitrate at − 5°. The sole product is 6-nitrotetrahydrocarbazole melting at 174°, since it is identical with the substance which results from the action of dilute acids on *cyclo*hexanone-*p*-nitrophenylhydrazone. Additional evidence in support of this view of its constitution was obtained in the following way.

The nitro-derivative, on reduction, yields 6-*aminotetrahydrocarbazole*, which melts at 152° and yields an acetyl derivative melting at 208°, and these substances have been synthesised by the following steps. p-*Acetylaminophenylhydrazine*,

$$CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot NH \cdot NH_2,$$
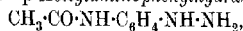
prepared from *p*-aminoacetanilide by diazotisation and reduction, condenses readily with *cyclo*hexanone, yielding *cyclo*hexanone-p-*acetylaminophenylhydrazone* (m. p. 166°), and this substance, when digested with glacial acetic acid, is converted into 6-*acetylaminotetrahydrocarbazole* (m. p. 208°), which was found to be identical

with the derivative of this composition obtained from the product of the nitration of tetrahydrocarbazole. On hydrolysis, it yielded 6-*aminotetrahydrocarbazole* melting at 152°.

Unexpected results were obtained in a series of experiments on the nitration of 9-acetyltetrahydrocarbazole (IV) in acetic acid solution. The product of nitration is a single *acetylnitrotetrahydro-carbazole* which melts at 174° and, on hydrolysis, yields a new *nitrotetrahydrocarbazole* melting at 172°. It was at first thought that the latter was identical with the 6-nitro-derivative (m. p. 174°), but this was shown not to be the case, (i) by a mixed melting point determination, and (ii) by preparing the *acetyl* derivative of 6-*nitro-tetrahydrocarbazole*, which was found to melt at 244° instead of 174°.

It is certainly remarkable that the action of nitric acid on the acetyl derivative should lead to the introduction of the nitro-group into a different position from that which it takes up when tetra-hydrocarbazole itself is nitrated. With regard to the constitution of the acetyl derivative of the new nitrotetrahydrocarbazole, two formulæ only are possible for reasons given below, namely, V and VI.

(V.)   (VI.)
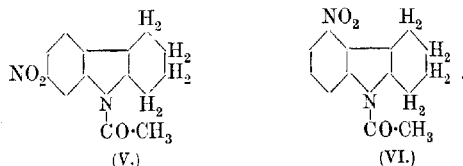
The question has an important bearing on the difficult problem of the nature of the nitrotetrahydrocarbazole which is formed from *cyclo*hexanone-*m*-nitrophenylhydrazone by the action of dilute acids. We have repeated the experiments of Borsche, Witte, and Bothe (*loc. cit.*, p. 68) and have satisfied ourselves that the action of dilute sulphuric acid on this *m*-nitrophenylhydrazone leads to the formation of a single nitrotetrahydrocarbazole (m. p. 154°) and not to a mixture of isomerides. The above-named investigators assign the 7-nitro-structure to this substance, and we are inclined to agree with their view that it is 7-*nitrotetrahydrocarbazole*.

It is, of course, conceivable that the *m*-nitrophenylhydrazone might yield 5-nitrotetrahydrocarbazole, but this, in our view, is probably the constitution of the isomeride which results from the nitration of 9-acetyltetrahydrocarbazole. Unfortunately, the experimental data available at the present time are not sufficient to allow of a decision as to the actual formula either of the product of the nitration of 9-acetyltetrahydrocarbazole or of the nitro-derivative formed from *cyclo*hexanone-*m*-nitrophenylhydrazone by the action of dilute sulphuric acid.

After the unexpected results which have been obtained in the nitration of 9-acetyltetrahydrocarbazole, it was thought that it would be interesting to investigate the nitration of a derivative of tetrahydrocarbazole containing a different radicle attached to the nitrogen atom, and for this purpose, 9-*methyltetrahydrocarbazole* (VII) was selected.

(VII.)   (VIII.)
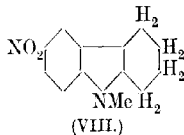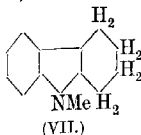
This substance, which appears to be new, was obtained by combining *as*-phenylmethylhydrazine, $C_6H_5\cdot NMe\cdot NH_2$, with *cyclo*hexanone and then digesting the resulting *cyclohexanonephenylmethylhydrazone* with dilute sulphuric acid. 9-*Methyltetrahydrocarbazole* melts at 50° and, on nitration, readily yields 6-nitro-9-methyltetrahydrocarbazole (VIII, m. p. 192°). That the nitrogroup in this substance occupies the 6-position was proved in the following way. On reduction, it yields 6-*amino-9-methyltetrahydrocarbazole* (m. p. 105°), the acetyl derivative of which melts at 238°. In order to synthesise this substance, *p*-aminomethylaniline was acetylated and the p-*acetylaminomethylaniline* converted into p-*acetylaminonitrosomethylaniline*, $CH_3\cdot CO\cdot NH\cdot C_6H_4\cdot NMe\cdot NO$, by means of nitrous acid. This, on reduction with zinc dust and acetic acid, yielded p-*acetylaminophenylmethylhydrazine*, $CH_3\cdot CO\cdot NH\cdot C_6H_4\cdot NMe\cdot NH_2$, which combined readily with *cyclo*hexanone.

The *cyclohexanone*-p-*acetylaminophenylmethylhydrazone* was then boiled with glacial acetic acid, when it yielded 6-*acetylamino-9-methyltetrahydrocarbazole*, which melted at 238° and proved to be identical with the substance of this composition obtained from the direct nitration of 9-methyltetrahydrocarbazole in the way described above.

During the course of these experiments, we were anxious to ascertain whether the presence of substituents in the 2- and 5-positions in phenylhydrazine would, by steric hindrance, prevent the Fischer indole synthesis from taking place, and we selected for experiment, 2-*chloro-5-nitrophenylhydrazine* (IX).

(IX.)   (X.)

3 R 2
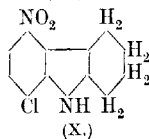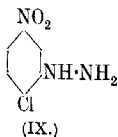
This substance, which does not appear to have been described, was made as follows. *o*-Chloroaniline, on nitration in concentrated sulphuric acid solution, yields 2-chloro-5-nitroaniline which, when diazotised and reduced with stannous chloride, is converted into 2-chloro-5-nitrophenylhydrazine (m. p. 160°). This combines readily with *cyclo*hexanone, and the resulting *cyclo*hexanone. 2-*chloro-5-nitrophenylhydrazone* (m. p. 78°) reacts readily with hot dilute sulphuric acid, yielding 8-*chloro-5-nitrotetrahydrocarbazole* (X), which crystallises in orange prisms melting at 214°. This rather unexpected result shows that the occupation of the 2- and 5-positions in phenylhydrazine does not inhibit tetrahydrocarbazole formation.

The new carbazole derivatives which have been synthesised during the course of this investigation from *cyclo*hexanone are in all cases derivatives of tetrahydrocarbazole, and it seemed desirable to endeavour to discover some process of oxidation which would remove the additional hydrogen atoms and yield the corresponding derivatives of carbazole. The information thus obtained would also be valuable in deciding the constitution of some nitro- and other derivatives of carbazole as to which there is still some doubt.

Borsche, Witte, and Bothe (*Annalen*, 1908, **359**, 75) heated tetrahydrocarbazole and several of its methyl derivatives with lead oxide at a high temperature and obtained small yields of carbazole and the corresponding methyl derivatives, but such a process is obviously inapplicable to the nitro- or halogeno-derivatives of tetrahydrocarbazole. During the investigation of harmine and harmaline, Perkin and Robinson (T., 1919, **115**, 961) showed that tetrahydroharmine, $C_{13}H_{16}ON_2$, is converted into harmaline, $C_{13}H_{14}ON_2$, when it is oxidised with permanganate. We were unsuccessful when we attempted to obtain dihydrocarbazole or carbazole from tetrahydrocarbazole by a similar process. An oxidising agent which has proved valuable in cases of this kind i mercuric acetate, thus, for example, tetrahydroepiberberine i readily oxidised to epiberberine by this reagent with the loss c four atoms of hydrogen (Perkin, T., 1918, **113**, 515). On investigat ing the behaviour of tetrahydrocarbazole and 9-methyltetrahydr carbazole towards mercuric acetate, we find that oxidation take place readily with the formation of carbazole and 9-methylcarbazol although the yields at present are not good. There are indicatio that this process may also be successfully applied in the case halogeno- and nitro-derivatives of tetrahydrocarbazole, and tl point is being investigated.

EXPERIMENTAL.

Tetrahydrocarbazole, $C_{12}H_{13}N$ (I).

In preparing this substance, Borsche (*Annalen*, 1908, **359**, 60) combines *cyclo*hexanone with phenylhydrazine and boils the resulting hydrazone with dilute sulphuric acid, but the product obtained in this way is always impure and pink-coloured. We find that a purer product is obtained direct when the hydrazone is boiled for a few minutes with five times its weight of glacial acetic acid, from which it separates, on cooling, as a mass of crystals melting at 119°, whereas Borsche gives 116° as the melting point.

The *picrate* separates, when a hot alcoholic solution of tetrahydrocarbazole is mixed with alcoholic picric acid, in dark red crystals melting at 147°, and recrystallisation from alcohol does not alter this melting point. Padoa and Chiaves (*Atti R. Accad. Lincei*, 1907, [v], **16**, 765) give the melting point of a specimen of the picrate prepared from tetrahydrocarbazole obtained by the reduction of carbazole as 133°, but most probably their tetrahydrocarbazole contained some unchanged carbazole.

9-Acetyltetrahydrocarbazole (IV).—The *cyclo*hexanoneacetylphenylhydrazone used in the preparation of this substance was obtained by heating *cyclo*hexanonephenylhydrazone with an equal weight of freshly-distilled acetic anhydride on the steam-bath for two hours and then distilling under reduced pressure, when the acetyl derivative passed over at 210—220°/14 mm. as a viscous liquid which did not crystallise (Found : $N = 12 \cdot 1$. $C_{14}H_{18}ON_2$ requires $N = 12 \cdot 2$ per cent.).

When this acetyl-hydrazone was heated with dilute sulphuric acid (20 per cent.) for a few minutes, an oil resulted which solidified on cooling. This product was recrystallised from alcohol, from which it separated in thick prisms melting at 77°, and this proved to be pure *9-acetyltetrahydrocarbazole*. In this particular case it was found rather unexpectedly that the closing of the indole ring, by boiling with acetic acid, occurred with some difficulty, and even after boiling for an hour some acetyl-hydrazone remained unchanged. The same acetyl derivative was obtained by the direct acetylation of tetrahydrocarbazole under the following conditions : Tetrahydrocarbazole (30 grams) was mixed with glacial acetic acid (150 c.c.) and acetyl chloride (50 c.c.), and after adding a little copper powder, the whole was allowed to remain for fourteen days in a flask fitted with a calcium chloride tube. The product was decomposed by ice and water, the sticky, dark green solid extracted with chloroform, the extract dried over calcium chloride, the chloroform removed, and the residue distilled under reduced pressure,

when an almost colourless distillate was obtained which solidified on cooling. This separated from alcohol in colourless crystals melting at 77°, and proved to be identical with the 9-acetyltetrahydrocarbazole obtained from the acetyl-hydrazone as explained above (Found : N = 6·5. $C_{14}H_{15}ON$ requires N = 6·6 per cent.).

This acetyl derivative may also be obtained by boiling tetrahydrocarbazole with three times its weight of acetic anhydride for six hours and then distilling the product. Several attempts were made to prepare 9-benzoyltetrahydrocarbazole from tetrahydrocarbazole by the action of benzoyl chloride under varying conditions, but the product was always resinous and could not be purified. Similar results were obtained when benzoic anhydride was used. If the solution of tetrahydrocarbazole in glacial acetic acid is boiled with benzoyl chloride in the presence of a little copper powder, and the product distilled, a solid is obtained which after crystallisation melts at 77° and consists of 9-acetyltetrahydrocarbazole.

The Nitration of Tetrahydrocarbazole.

6-Nitro- and 6-Amino-tetrahydrocarbazole.

It is explained in the introduction (p. 1827) that the nitration of tetrahydrocarbazole may be directly accomplished at low temperatures, and the following conditions have been found to work well :

Tetrahydrocarbazole (10 grams), dissolved in concentrated sulphuric acid (70 c.c.), is cooled to − 5° and then the theoretical quantity (5·9 grams) of powdered potassium nitrate added in small quantities at a time, the solution being continuously stirred and kept below − 3°. The product is poured on to ice, the crude, yellow nitro-compound collected, washed thoroughly with water, and dried over sulphuric acid. It is then recrystallised from alcohol, from which it separates in small, thick prisms melting at 174°, and careful comparison showed that this substance is identical with the nitrotetrahydrocarbazole obtained by Borsche (Annalen, 1908, **359**, 67) from cyclohexanone-p-nitrophenylhydrazone by warming with sulphuric acid.

The 9-Acetyl Derivative.—This substance, which was required for comparison with the acetyl derivative obtained by nitrating acetyltetrahydrocarbazole (compare p. 1828), was prepared in the following manner. 6-Nitrotetrahydrocarbazole (5 grams) was boiled with acetic anhydride (50 c.c.) for two hours, when, on cooling, yellow needles separated, which were recrystallised from glacial acetic acid (Found : N = 10·8. $C_{14}H_{14}O_3N_2$ requires N = 10·8 per cent.).

6-*Nitro*-9-*acetyltetrahydrocarbazole* melts at 244° and is readily hydrolysed to 6-nitrotetrahydrocarbazole when it is digested with a solution of sodium hydroxide in 50 per cent. aqueous alcohol.

6-*Aminotetrahydrocarbazole*.—In order to prepare this substance, the nitro-derivative (4 grams) was added to a mixture of iron filings (10 grams), water (100 c.c.), and hydrochloric acid (3 c.c.) and the whole heated on the steam-bath for an hour with frequent shaking. The product was cooled, made alkaline with sodium hydroxide, and the solid collected and extracted several times with boiling water, when, on cooling, the amino-derivative separated in crystals, the yield being about 40 per cent. of the theoretical.

6-*Aminotetrahydrocarbazole* separates from alcohol or toluene in colourless plates and melts at 152° (Found : $N = 15\cdot1$. $C_{12}H_{14}N_2$ requires $N = 15\cdot0$ per cent.). The picrate was prepared by mixing the hot alcoholic solution of the amino-derivative (1 gram) with picric acid (1·2 grams), when, on cooling, bright red needles separated which, after recrystallisation from alcohol, melted at 214° with decomposition.

6-*Acetylaminotetrahydrocarbazole* was prepared by mixing the amino-derivative in hot benzene with a slight excess of acetic anhydride. The crystalline mass was collected and recrystallised from dilute acetic acid, from which it separated in thick, colourless prisms melting at 208°.

6-*Benzoylaminotetrahydrocarbazole* was precipitated when the amino-derivative, dissolved in hot benzene, was mixed with benzoyl chloride, and separated from alcohol in clusters of short prisms melting at 207° (Found : $N = 9\cdot6$. $C_{19}H_{18}ON_2$ requires $N = 9\cdot7$ per cent.).

Synthesis of 6-*Acetylaminotetrahydrocarbazole*.—For the purpose of this synthesis, *p*-acetylaminophenylhydrazine hydrochloride was prepared from *p*-aminoacetanilide by reduction with stannous chloride in the usual manner (Riedel, D.R.-P. 80843) and was employed as such because the free base is difficult to obtain pure and rapidly decomposes on standing in the air. Sodium (5 grams) dissolved in alcohol (80 c.c.) was mixed with *cyclo*hexanone (6·5 grams) and the hydrazine hydrochloride from 10 grams of *p*-amino-acetanilide added, when there was considerable rise of temperature. The whole was warmed on the steam-bath for a few minutes, mixed with water, the precipitate collected and recrystallised from alcohol, from which it separated in needles melting at 165—166°, and this substance, which decomposed gradually on keeping, is *cyclo*hexanone-*p*-*acetylaminophenylhydrazone* (Found : $N = 17\cdot1$. $C_{14}H_{19}ON_3$ requires $N = 17\cdot1$ per cent.). When an attempt was made to convert this substance into the corresponding indole

derivative by the action of sulphuric or hydrochloric acid, simul-
taneous elimination of the acetyl group took place.

It was, however, found that glacial acetic acid leads directly and
easily to 6-acetylaminotetrahydrocarbazole. The hydrazone was
simply heated with glacial acetic acid almost to the boiling point,
the flame was then removed, when the formation of the indole ring
took place so energetically that the acid boiled for some time.
On the addition of a little water, 6-*acetylaminotetrahydrocarbazole*
separated from the dilute acetic acid in short, colourless prisms
melting at 208° (Found : $N = 12·5$. $C_{14}H_{16}ON_2$ requires $N = 12·3$
per cent.). The free amino-derivative was obtained by boiling
the acetyl derivative with concentrated hydrochloric acid for ten
minutes, during which time the hydrochloride separated as a
gelatinous precipitate. The whole was mixed with ice, made
alkaline with ammonia, and the amino-derivative collected, washed,
dried, and recrystallised from alcohol, from which it separated in
small plates melting at 152°. A careful comparison showed that
this base (and its acetyl derivative) is identical with 6-aminotetra-
hydrocarbazole (and its acetyl derivative) prepared from 6-nitro-
tetrahydrocarbazole by reduction in the manner described above.

9-*Methyltetrahydrocarbazole* (VII) *and its* 6-*Nitro-* (VIII) *and* 6-
Amino-derivatives.

9-Methyltetrahydrocarbazole, which does not appear to have
been described, may be obtained from *cyclo*hexanone and aa-
phenylmethylhydrazine in the following manner : The phenyl-
methylhydrazine (5 grams) is mixed with *cyclo*hexanone (4·1 grams),
when there is a considerable rise of temperature and the mixture
becomes cloudy owing to the separation of water.

After heating on the steam-bath for a few minutes, the hydrazone
is converted into the carbazole by boiling with sulphuric acid
(20 c.c.) and water (90 c.c.), when an oil separates which crystallises
on cooling, and on recrystallisation from alcohol 9-methyltetra-
hydrocarbazole separates in colourless needles. Alternatively, the
hydrazone is boiled with glacial acetic acid for a few minutes, when,
on diluting with water, the carbazole separates as an oil which
soon solidifies and is again crystallised from alcohol (Found :
$N = 7·5$. $C_{13}H_{15}N$ requires $N = 7·6$ per cent.).

9-*Methyltetrahydrocarbazole* melts at 50° and yields a picrate
which separates from alcohol in dark red needles melting at 116°.

6-*Nitro-9-methyltetrahydrocarbazole* was obtained in almost quan-
titative yield by the method used in the case of the preparation
of 6-nitrotetrahydrocarbazole, and the crude product was crystallised

rom glacial acetic acid, from which it separated in long, yellow prisms melting at 192° (Found : N = 12·2. $C_{13}H_{14}O_2N_2$ requires N = 12·2 per cent.).

6-*Amino*-9-*methyltetrahydrocarbazole* was prepared by reducing the nitro-derivative with iron and a little hydrochloric acid (compare p. 1829), and the product was extracted with boiling water, when, on cooling, the amino-derivative separated in colourless prisms melting at 105°.

The *picrate* crystallises from hot alcohol in orange needles and melts at 212° (Found : N = 16·1. $C_{13}H_{16}N_2,C_6H_2(OH)(NO_2)_3$ requires N = 16·3 per cent.).

6-*Acetylamino*-9-*methyltetrahydrocarbazole* is readily obtained by adding acetic anhydride to the solution of the amino-compound in benzene and is purified by crystallisation from acetic acid, from which it separates in colourless needles melting at 238° (Found : N = 11·6. $C_{15}H_{18}ON_2$ requires N = 11·6 per cent.).

Synthesis of 6-*Acetylamino*-9-*methyltetrahydrocarbazole*.—For the purpose of this synthesis, *p*-aminomethylaniline, $NH_2 \cdot C_6H_4 \cdot NHMe$, was prepared by the reduction of *p*-nitrosomethylaniline with sodium sulphide. This was dissolved in benzene and treated with the theoretical amount of acetic anhydride, when there was considerable rise of temperature and *p*-acetylaminomethylaniline separated as an oil. This was extracted and separated from the benzene by the calculated quantity of dilute hydrochloric acid, the solution was cooled below 0°, and the required amount of sodium nitrite, dissolved in a little water, added gradually with continuous stirring. The *p*-*acetylaminonitrosomethylaniline*, $CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot NMe \cdot NO$, which separated in rather poor yield as a yellow, crystalline mass, was collected, washed with water, and recrystallised from alcohol, from which it separated in almost colourless plates and melted at 146° (Found : N = 21·7. $C_9H_{11}O_2N_3$ requires N = 21·8 per cent.). This acetyl derivative (4 grams) was made into a paste with glacial acetic acid (6 grams) and gradually added to water (21 c.c.) and zinc dust (12 grams of 90 per cent.) with continuous stirring, when there was some rise of temperature, which, however, was kept below 25°.

After remaining over-night, the product was rendered alkaline by the addition of sodium hydroxide, extracted with much ether, the ethereal solution dried over potassium carbonate, and evaporated, when *p*-*acetylaminophenylmethylhydrazine*,

$$CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot NMe \cdot NH_2,$$

remained as a dark oil.

This oil was now added to excess of *cyclo*hexanone, and the resulting hydrazone boiled with glacial acetic acid (10 grams),

3 R*   •

when the formation of the indole ring proceeded smoothly, and on the addition of water, 6-*acetylamino*-9-*methyltetrahydrocarbazole* was precipitated. After crystallisation from acetic acid, this melted at 238° (Found : N = 11·5. $C_{15}H_{18}ON_2$ requires N = 11 per cent.) and was shown to be identical with the substance of this composition obtained from the product of the nitration of 9-methyl tetrahydrocarbazole (p. 1835) by careful comparison and by the fact that the mixture of the two preparations melted at 238°.

5(?)-*Nitrotetrahydrocarbazole.*

Although tetrahydrocarbazole and 9-methyltetrahydrocarbazole on nitration under the conditions given on pp. 1832 and 1834, give almost quantitative yields of the corresponding nitro-derivative in which the nitro-group occupies the 6-position, 9-acetyltetra hydrocarbazole behaves quite differently. When nitration was attempted in sulphuric acid solution with potassium nitrate, an unsatisfactory product was obtained, from which nothing definite could be isolated by recrystallisation from the usual solvents.

It was, however, ultimately discovered that nitration may be satisfactorily carried out in glacial acetic acid solution under the following conditions. 9-Acetyltetrahydrocarbazole (3·6 grams) was dissolved in glacial acetic acid (50 c.c.) and then nitric acid (1·7 grams of d 1·4) diluted with a little glacial acetic acid gradually added at room temperature. The mixture was allowed to remain over-night, when long, pale yellow prisms separated which were collected and recrystallised from glacial acetic acid (Found : N = 10·7. $C_{14}H_{14}O_3N_2$ requires N = 10·8 per cent.).

5-*Nitro*-9-*acetyltetrahydrocarbazole* melts at 174° and is readily hydrolysed when it is warmed with a solution of sodium hydroxide in 50 per cent. aqueous alcohol. On the addition of water, a yellow, crystalline substance separates which may be crystallised either from alcohol or chloroform, from which it separates in long prisms (Found : C = 66·6 ; H = 5·6 ; N = 12·9. $C_{12}H_{12}O_2N_2$ requires C = 66·6 ; H = 5·5 ; N = 13·0 per cent.).

5-*Nitrotetrahydrocarbazole* melts at 172°, or at about the same temperature as the 6-nitro-derivative, and as it was at first thought that these two substances might be identical, a mixed melting-point determination was made, when the mixture began to melt at 125° and was completely melted at 151°.

7(?)-*Nitrotetrahydrocarbazole* and 8-*Chloro*-5-*nitrotetrahydrocarbazole* (X).

It has already been pointed out (p. 1828) that the action of *m*-nitrophenylhydrazine on *cyclo*hexanone might theoretically lead

to the formation of 7-nitro- or 5-nitro-tetrahydrocarbazole or a mixture of both, and the following experiment was made with the object of ascertaining whether the product is actually a single substance or a mixture of isomerides. cycloHexanone-m-nitrophenylhydrazone (5·4 grams) was mixed with sulphuric acid (10 c.c.) and water (50 c.c.), in which it dissolved, but, on boiling, a brickred, crystalline precipitate separated which was collected, washed with water, and dried. The yield of this substance was 82 per cent. of that theoretically possible, the loss being due to the hydrolysis of a little of the hydrazone into m-nitrophenylhydrazine and cyclohexanone. In this condition, the substance melted at 154°, and this was not altered by recrystallisation from methyl alcohol, from which the substance separated in clusters of prisms and was obviously homogeneous. Although carefully searched for, no trace of any isomeride of this 7-nitrotetrahydrocarbazole could be detected.

8-Chloro-5-nitrotetrahydrocarbazole (compare p. 1829).—The preparation of this interesting substance was carried out under the following conditions. 2-Chloro-5-nitroaniline was prepared from o-chloroaniline by nitration in concentrated sulphuric acid solution, under the conditions recommended by Chattaway, Orton, and Evans (Ber., 1900, **33**, 3062). This substance (6 grams) was added to concentrated hydrochloric acid (50 c.c.) and diazotised below 0° by the addition of sodium nitrite (2·5 grams) dissolved in a little water. A solution of stannous chloride (15·5 grams) in concentrated hydrochloric acid (20 c.c.) was then added, and the precipitate collected, washed with a little water, dissolved in much hot water, and the tin removed by means of hydrogen sulphide. The free 2-chloro-5-nitrophenylhydrazine was obtained from the filtrate by the addition of sodium acetate and was recrystallised from alcohol, from which it separated in .long, orange needles melting at 160° (Found : N = 22·5. $C_6H_6O_2N_3Cl$ requires N = 22·4 per cent.).

cycloHexanone (1·3 grams) and 2-chloro-5-nitrophenylhydrazine (2 grams) were mixed together in boiling alcoholic solution, when, on cooling, cyclohexanone-2-chloro-5-nitrophenylhydrazone separated in bright yellow prisms melting at 78° (Found : N = 15·7. $C_{12}H_{14}O_2N_3Cl$ requires N = 15·7 per cent.). The influence on the colour due to the introduction of the chlorine atom is very marked, since cyclohexanone-m-nitrophenylhydrazone is bright red.

The hydrazone (2 grams) was now heated with sulphuric acid (4 c.c.) and water (20 c.c.), when 8-chloro-5-nitrotetrahydrocarbazole separated as a reddish-brown solid, which was purified by recrystallisation from alcohol, from which it separated in clusters of orange

3 R* 2

prisms melting at 214° (Found : $N = 11.3$. $C_{12}H_{11}O_2N_2Cl$ requires $N = 11.2$ per cent.).

Oxidation of Tetrahydrocarbazole and of 9-Methyltetrahydrocarbazole.

The interest attaching to the oxidation of hydrocarbazole derivatives is discussed in the introduction (p. 1830), and one of the objects we had in view was the discovery of a process which would be applicable, not only to the hydrocarbazoles themselves, but also to the chloro-, nitro-, and other derivatives. In the first experiments, the oxidation of tetrahydrocarbazole, suspended in dilute sulphuric acid at room temperature, with the theoretical quantity of permanganate was investigated. Oxidation took place very readily with almost immediate disappearance of the pink colour, but no carbazole could be isolated from the product. A similar negative result was obtained when tetrahydrocarbazole, without solution in dilute sulphuric acid, was oxidised with aqueous permanganate at about 80°. Subsequent experiments seemed to indicate that mercuric acetate may prove to be a useful reagent in such oxidations, as the following examples show.

Oxidation of Tetrahydrocarbazole to Carbazole.—This change takes place under the following conditions. Tetrahydrocarbazole (5 grams) is dissolved in glacial acetic acid (25 c.c.) at 85° and the solution added to the theoretical quantity of mercuric oxide (25·5 grams), dissolved in glacial acetic acid (25 c.c.), also at 85°. The mixture is heated on the steam-bath for a few minutes, allowed to cool, the mercurous acetate removed by filtration, and the filtrate diluted with water, when a yellow mercury compound of unknown composition separates. This was collected with the aid of the pump, washed with dilute nitric acid, and dried on porous porcelain. Hydrogen sulphide was now bubbled through this mercury derivative suspended in hot glacial acetic acid (50 per cent.), and the whole filtered hot, when, on dilution with water, the filtrate gave a small quantity of a solid which, after crystallisation from toluene, proved to be *carbazole*, but the yield was small.

Oxidation of 9-Methyltetrahydrocarbazole to 9-Methylcarbazole.

In this experiment, the oxidation with mercuric acetate was carried out under the conditions stated in the case of the oxidation of tetrahydrocarbazole and on diluting the filtrate from the mercurous acetate with water a sticky mass separated. This was extracted with chloroform, the solution dried over calcium chloride, the chloroform removed, and the residue distilled under 23 mm.

pressure, when metallic mercury and a colourless oil collected in the receiver. The oil soon solidified and, after crystallisation from alcohol, melted at 85—86° and proved to be 9-*methylcarbazole*, as a comparison of the properties and a mixed melting-point determination demonstrated. The yield was better than in the tetrahydrocarbazole experiment, and amounted to at least 20 per cent. of the theoretical.

Lastly, an experiment was made on the action of mercuric acetate on 6-nitrotetrahydrocarbazole, and in this case also mercurous acetate was formed; and water precipitated from the acetic acid filtrate a mercury derivative, the investigation of which is in progress.

THE DYSON PERRINS LABORATORY,
        OXFORD.   [*Received, October* 1st, 1921.]

CCX.—*Some Properties of Fused Sodium Hydroxide.*

By THOMAS WALLACE and ALEXANDER FLECK.

THE amount of information available concerning fused sodium hydroxide is very small considering the enormous quantities which are produced and used every day in the chemical industry.

Certainly for one period in its production, and often continuously in its use sodium hydroxide is in the fused condition, and as such possesses many characteristic chemical properties, some of which are quite distinct from the properties of sodium hydroxide in solution.

This paper is a collection of some results obtained in the course of everyday working and experimenting with the fused material. It is divided into three sections.

Section A.—Estimation of moisture contained in sodium hydroxide.

Section B.—Action between sodium hydroxide and metals when heated in air.

Section C.—Action between metals and mixtures of sodium hydroxide and sodium peroxide.

A.—Estimation of the Moisture contained in Sodium Hydroxide.

The fact that sodium hydroxide, even when fused, contains moisture is quite well known, and various methods are available for removing it. Among these are

(1) The addition of sodium.

(2) Prolonged heating at 700° (Neuman and Bergve, *Zeitsch. Elektrochem.*, 1915, **21**, 143).

(3) Electrolytic decomposition.

None of these methods is easily applicable for a quantitative estimation. The suggestion of a suitable method came from some observations made when sodium hydroxide was being fused in a vacuum. An iron boat containing this material was placed in a horizontal glass tube connected with a mercury pump. The apparatus was evacuated and the sodium hydroxide slowly fused. As soon as the hydroxide melted, an extraordinarily vigorous bubbling and spitting took place. So much sodium hydroxide was thrown from the boat that the glass tube became quite opaque. This continued for some time, and then the alkali which was left in the boat became quiet, and it was seen that in the cooler portions of the tube moisture had condensed. By weighing the sodium hydroxide used and by absorbing the water in a weighed phosphoric

FIG. I.

(a) *Silica tube.* (b) *Metal tube and boat.* (c) *Glass plugs.* (d) *Airtight sealing-wax joints.* (e) *Phosphoric oxide tube with pressure-tubing joints* (c_1c_1). (f) *Portion of tube heated.*

oxide tube, the percentage of moisture could easily be obtained. This method with some modifications was used and the arrangement is shown in Fig. 1. A silica tube was used to minimise the risk of cracking. A metal tube was introduced in order to protect the silica, and the rounded glass plug with which the tube was sealed enabled a view of the boat to be obtained. The sodium hydroxide used, which had been fused for some weeks before being poured into the boat, was weighed with all possible speed. By handling the hydroxide quickly while it was warm, it could be got into the tube without taking any appreciable quantity of moisture from the air. When the boat had been placed in the tube and the apparatus evacuated, the tube was gradually heated to approximately 500° and this temperature was maintained for about an hour. Long before this time had elapsed all ebullition had ceased. After the apparatus had cooled, the phosphoric oxide tube was detached and weighed. It was found that the amount of moisture varied in different samples of sodium hydroxide. The lowest value observed was 0·9, the highest was 1·2, whilst the average value was 1·1 per cent.

It is interesting to note that if white, crystalline sodium hydroxide is put into the boat at the beginning, it will still be white at the end of the experiment. Had the fusion at 500° taken place in an iron boat in air, the sodium hydroxide would have become distinctly green. It was further observed that when green sodium hydroxide has been put into the boat initially, the hydroxide which remains in the boat at the end of the experiment has become pure white. These observations indicate :

(a) That air (or oxygen) is necessary to effect any solvent action between iron and sodium hydroxide at temperatures up to 500°.

(b) That in a vacuum, iron is capable of acting as a reducing agent in fused sodium hydroxide in the same way as sulphur, sodium, etc.

B.—Reaction between Sodium Hydroxide and Metals when Heated in Air.

Analysis of sodium hydroxide, even of the white, finished product, always reveals the presence of metallic impurities, usually oxides of iron, aluminium, nickel, manganese, calcium, and magnesium.

Sodium hydroxide fused in an iron vessel is invariably coloured, due to these metallic impurities (except immediately after treatment with some reducing agent, usually sulphur). The colour of the sodium hydroxide varies with the temperature and the relative proportion of metals dissolved. For example, if iron is predominant, then the sodium hydroxide has a green colour up to about 450—500°. At higher temperatures, it becomes blackish-yellow. If copper is predominant, the sodium hydroxide is coloured an intense blue, and so on.

It is interesting to note, in passing, that the amount of metals in solution is always very small, and that a very small percentage of metallic impurity produces a very strong coloration in the sodium hydroxide.

We have had occasion to examine many samples of commercial sodium hydroxide, which were in most cases very pure so far as other sodium salts are concerned, and we have never found the total percentage of metallic oxides to be more than 0·05 per cent. The bulk of this is usually iron and manganese, yet these small quantities are sufficient to colour the sodium hydroxide very deeply. In order to obtain a more complete knowledge of the behaviour of fused sodium hydroxide with metals, we conducted the several series of experiments given below.

1. *Action of Fused Sodium Hydroxide on Iron at Various Temperatures.*

Two sets of experiments were performed :

(a) With spun iron laboratory crucibles.

(b) With cast crucibles made from the iron used in the manu-facture of ordinary melting pots for sodium hydroxide.

The sodium hydroxide used was of the best quality, never con-taining more than 1 per cent. of total impurity, of which the greatest part was sodium carbonate. The hydroxide was in the form of large, glistening crystals taken from the middle of a large mass, and small pieces of these were placed in the crucible.

The apparatus used is shown in Fig. 2, and with these arrange-ments it was possible to keep the temperature fairly constant to within 10°.

FIG. 2.

(a) *Firebricks.*   (b) *Iron pot.*   (c) *Iron crucibles.*   (d) *Gas ring.*
(p) *Pyrometer.*
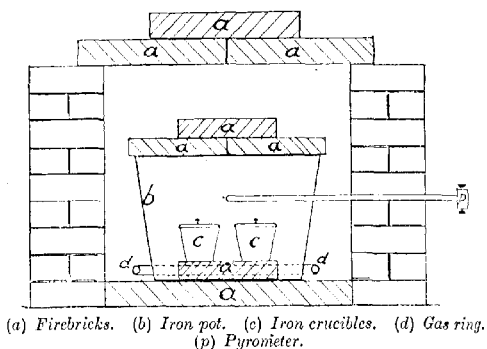
The *modus operandi* was the same throughout the experiments. Two crucibles were placed in the furnace together and were used, when possible, throughout the series. Before each experiment, the insides of the crucibles were cleaned and burnished. Fifty grams of solid sodium hydroxide were introduced, and the crucibles were covered by loose lids, placed in the furnace, and kept at the required temperature for four hours. By heating the furnace to the required temperature before the crucibles were put in, a steady condition could be obtained within an hour.

At the end of four hours the crucibles were removed and the contents poured into nickel moulds. Each crucible was then thoroughly washed out and the washings were added to the solution of the main quantity of the sodium hydroxide. The total iron in the resulting liquid was estimated. Wherever possible, the amount

Temp.	No. of expts.	Frequency.	Colour of fused sodium hydroxide.	Condition.	Cooling phenomena.	Suspended matter.	Residue.	Iron in solution per cent.	Grains of iron removed from the crucible.
350°	9	8	Colourless.		—	Red iron oxide.	None.	—	0·4
		1	"		—	None.	"	—	—
400	8	6	Pale green.	Very turbid.	—	Red iron oxide.	"	—	0·425
		2	"	Crystal clear.	—	" "	"	—	0·425
450	8	8	Green.	Quite clear.	—	None.	Red iron oxide.	0·02-0·04	0·2-0·3
500	6	4	Almost colourless.	Clear.	Became turbid owing to the formation of a yellow ppte. as the hydroxide cooled.	"	Very small amount of red oxide.	0·011-0·024	0·2-0·3
		2	Bright green.	"	No ppte.	"	"	0·018-0·028	0·2-0·3
550	8	3	Almost colourless.	"	Became turbid owing to the formation of a yellow ppte. as the hydroxide cooled.	Small yellow crystals resembling lead iodide crystallised from water.	"	0·02	0·4-0·48
		5	Dark greenish-brown.	Almost opaque.	No ppte. seen.	None.	"	0·048	0·09
600	6	5	Dark yellowish-green.	"	" "	Large quantity of crystals.	None.	0·068	0·3
		1	Dark brown.	"	" "	Very few crystals.	"	0·068	0·13
650	1	1	Dark yellowish-green.	Opaque.	" "	Large quantity of crystals.	Red iron oxide.		

Note.—One experiment was performed in which a crucible containing sodium hydroxide was heated to 350°. After four hours the contents were examined and found to be red and turbid. The furnace was closed and allowed to cool very slowly. The final product was a solid mass of white sodium hydroxide in which all the red oxide had collected at the bottom.

of iron dissolved in the sodium hydroxide was estimated inde-
pendently. The experiment was repeated three or four times at
each particular temperature.

Table I gives the observations and data collected from the experi-
ments conducted with laboratory crucibles. Particularly from
500° upwards, the action of sodium hydroxide and iron seems to
be very complex, and at each of the temperatures taken we were
met with absolutely different phenomena under what were, so far
as we knew, the same conditions. The term " Frequence " in the
table indicates for each particular temperature the number of times
the phenomena described were met with. We are without any
satisfactory explanation why this variation in the phenomena
occurred.

Results with Cast Iron Crucibles.

The qualitative results were the same as those described in the case
of spun crucibles, except in one particular. The sodium hydroxide
obtained at 550°, when dissolved in water, gave a large quantity
of purple precipitate, which yielded ferric hydroxide on keeping,
or on the addition of water and was probably sodium ferrate.
The total amount of iron removed was, however, much larger,
and on the whole the tendency seemed to be for the quantity to
rise with the temperature.

As in the previous experiments, the formation of the scintil-
lating crystals was associated with a considerable rise in the total
quantity of iron removed. The iron in solution was estimated
and the quantity found to be of the same order as that estimated
in the sodium hydroxide used with the other crucibles.

In generalising the results of these observations it should be
clearly understood that they might be different if a period of heating
other than four hours had been fixed upon. Practical experience,
however, has shown that, in these experiments, the quantities of
iron dissolved in the sodium hydroxide are of the same order as
those contained in hydroxide which has been fused in iron pots
for several weeks.

The quantitative results obtained with cast iron crucibles and
those given in the table, are shown graphically in Fig. 3.

The important conclusions to be drawn from the table and the
curves are as follows :

1. At temperatures up to and including 400° the ferric oxide
formed by the action of sodium hydroxide and iron remains in
suspension for at least several hours and practically no iron is
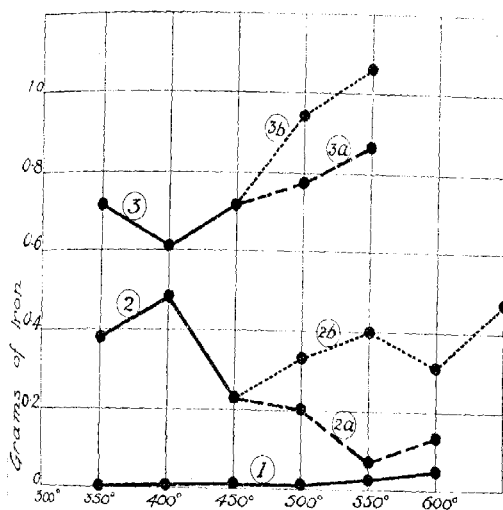dissolved.

2. Between 400° and 500° the amount of iron removed is much

smaller. The red oxide formed settles to the bottom very quickly, except for a small amount which dissolves in the sodium hydroxide.

3. Between 500° and 550°, a soluble substance is formed which settles out as a yellow precipitate when the sodium hydroxide cools. This does not always occur.

4. At 550° and above, a yellow, crystalline substance is formed which is insoluble in sodium hydroxide at temperatures up to 650°.

FIG. 3.

Laboratory iron crucibles.—(1) Quantity of iron dissolved.   (2) Quantity of iron removed (a) when yellow precipitate and crystals are not formed ; (b) when yellow precipitate and crystals are formed.

Cast iron crucibles.—(3) Quantity of iron removed (a) when yellow precipitate is not formed ; (b) when yellow precipitate is formed.

5. The graphs of the quantitative data show clearly that

(a) The amount of iron dissolved is very small compared with the amount removed.

(b) The amount dissolved increases with the temperature.

(c) With laboratory iron crucibles the amount removed falls rapidly from 400° to 600°, except when yellow crystals are formed. In these cases the amount is greatly increased.

(d) With cast iron crucibles the tendency is for the amount removed to increase steadily with rise of temperature.

Isolation of the Crystalline Substance observed at 550° and above.

By the methods described above, it was impossible to isolate an of the crystals, as they were spread through the mass of the soli sodium hydroxide obtained in the mould, and treatment wit water always gave a precipitate of ferric hydroxide, from whic the crystals could not easily be separated. A new method ha to be adopted.

The crucibles were treated exactly as before, the sodium hydr oxide was introduced, and the crucibles were heated to 500—60(and left for four to eight hours. The gas was then turned off, th crucibles left in the furnace to cool slowly, and, when cold, the soli block of sodium hydroxide was tapped out of the crucible. Th first result of this method was to reveal the presence of some dar
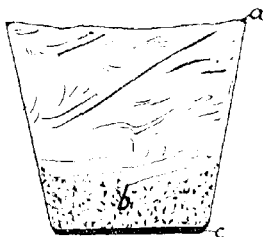
Fig. 4.

(a) *Red crystals.*   (b) *Yellow crystals.*   (c) *Red iron oxide.*

red crystals which had not been seen before. The solid block (hydroxide was split vertically and gave a section sketched in Fig. 4 It will be observed that the red oxide and the yellow crystals ha settled out very conveniently for purposes of separation, and tha the dark red crystals were found at the point where air, iron, an sodium hydroxide meet.

The bottom of the block was split off and a piece of sodiur hydroxide was thus obtained containing all the yellow crystal with a compact layer of red oxide on the bottom. This was con pletely scraped off with a knife, and the sodium hydroxide dissolve in water. A solution was obtained, with the yellow crystals an a small amount of the red oxide in suspension. The final separatio was accomplished by spinning the solution round and then holdin the beaker still. The red oxide rapidly settled out in a little hea on the bottom while the crystals were still carried round with th liquid. The latter was rapidly decanted off and carried the maje

portion of the crystals with it, while the red oxide was left in the beaker.

A sample of the dark red crystals was easily obtained by breaking off the sodium hydroxide at the edges, which was quite free from the red oxide, and dissolving it. Being at the edge, the crystals could be removed with only a very small amount of sodium hydroxide.

In this way a fairly large quantity of the yellow crystals was obtained, and a small quantity of the darker crystals. The yellow crystals consist of iron, sodium, and oxygen, and their chemical properties are identical with those of the red crystals described in p. 1854. The presence of sodium was first indicated in an attempt to estimate the oxygen by reduction in a stream of hydrogen. Very varying results were obtained, and in all cases the boat (both platinum and silica were used) showed signs of having been acted on. This disproved the suggestion that the yellow crystals might be crystalline oxides of iron.

The analysis of the crystals proved very unsatisfactory. The estimation of the iron was effected without difficulty, but even here the results obtained were never within the limits of experimental error, although they were always fairly close to one another. The estimation of the sodium was completely unsatisfactory, the difficulty being to obtain a suitable method. This difficulty was overcome later and the method finally employed to estimate the sodium will be fully dealt with in section C.

Several analyses were performed (Found : Fe $= 56\cdot3$; Na $= 14\cdot8$; $O = 28\cdot9$ per cent.), but the figures correspond with no simple formula ($Na_3Fe_5O_9$ is the simplest), and cannot be regarded as giving more than an indication of the composition of the crystals.

Owing to the trial of one method after another, our sample was almost exhausted. Our old crucibles were worn out, and we had to wait many months before new ones could be obtained (1917—18). When we did get them, we were totally unsuccessful in our attempts to prepare anything like reasonable quantities of the crystals. The reason for this is not evident. The matter was allowed to rest there until another series of experiments was performed, which is described in section C.

2. Action of Fused Sodium Hydroxide on Nickel at Various Temperatures.

Ordinary laboratory nickel crucibles were used, and the gas-fired furnace was replaced by an electrically-heated muffle. In each experiment two crucibles containing 150 grams of sodium hydroxide

TABLE II.

Observations made with Sodium Hydroxide and Nickel.

Temp.	No. of expts.	Frequence.	Colour of fused sodium hydroxide.	Condition.	Cooling phenomena.	Suspended matter and residue.	Nickel in the solution per cent.
			Series 1 with new crucibles.				
360°	8	4	Very pale green.	Clear.	Set to white solid with purple tint.	None.	0·01-0·02
		4	Pale green.	Clear, with slight scum.	Black ppte. on cooling.	,,	0·01-0·02
400	10	2	Colourless.	Clear.	No ppte.; set to pure white solid.	,,	Trace.
		5	Pale green.	Clear, with slight scum.	No ppte.; set to yellow solid.	,,	0·008
		1	Very pale green.	Clear.	—	Small quantity of small, silvery crystals floating in the sodium hydroxide.	0·014
		2	Greenish-yellow.	Clear, with scum.	Black ppte. on cooling.	—	0·02
			Series 2 with same crucibles as before.				
350	4	4	Green.	Clear, with scum.	Black ppte. on cooling.	—	0·01-0·03
375	6	6	,,	,, ,, ,,	,, ,, ,, ,,	—	0·01-0·03
400	4	4	,,	More scum.	,, ,, ,, ,,	—	0·01-0·02
450	4	4	,,	No scum.	Much less ppte.	—	0·01-0·02
500	6	6	,,	,, ,,	Very little ppte.	—	0·005-0·015

and fitted with fairly tight nickel lids were used. The nickel in the hydroxide was estimated by dissolving the product in hydrochloric acid and precipitating the nickel by dimethylglyoxime in the usual way. The phenomena observed were very inconsistent. Owing to this, one series of experiments was abandoned altogether, and another undertaken with the intention of raising the temperature by steps of 20° rather than 50°.

It is very difficult to sum up the reaction of nickel and sodium hydroxide. The most feasible line of explanation is that the inner surface of the crucible is oxidised in some way which is not very clear. It is well known that nickel oxide is only very slightly soluble in sodium hydroxide, and it would consequently form a protective covering. This would account for the small quantities of nickel found in the alkali and for the absence of anything comarable with the red oxide obtained with iron crucibles. The production of the silvery crystals observed in one isolated case will be ully dealt with in section C. In some cases, similar to what we nce or twice obtained with iron crucibles, there seemed to be no ction whatever. The explanation of such cases, in which the iside surface of the crucibles remained quite bright and clean, rould seem to be one where the metal was in the passive state. t should be noted, however, that these negative results were not ibtained after the crucibles had been used for a while.

3. Action with Copper at Various Temperatures.

A similar series of experiments to those performed with nickel xas undertaken with two crucibles beaten out of ⅛-inch sheet.

With copper there seemed to be a very complex action, judging by the various phenomena which were observed. In contradistinction to iron, the phenomena were almost the same for various temperatures, but they became intensified as the temperature rose.

The following phenomena were observed at 350°, and in a greater degree at higher temperatures.

The fused sodium hydroxide was clear and intensely blue and contained a number of shiny scales floating in it. On pouring the melt into a cold mould, the first sodium hydroxide to touch the mould instantly became intensely yellow, whilst the rest of the hydroxide, cooling comparatively slowly, deposited a red substance. The final solid was dark red, with a bright yellow surface where it had been in contact with the mould. This yellow effect was without doubt due to the sudden cooling of the sodium hydroxide.

Several interesting phenomena were observed during the analysis of the sodium hydroxide. When the alkali was put into water, a rivid yellow substance was precipitated, and this was followed by

the precipitation of a bright red powder. After keeping, the whole precipitate turned red. The solution itself was of a blue colour, which deepened on keeping. The copper was estimated by precipitation with hydrogen sulphide in the usual way after the addition of hydrochloric acid. This precipitation was somewhat curious. The hydrochloric acid solution was yellowish-green and gave a precipitate only very slowly with hydrogen sulphide, in fact, a few minutes elapsed before the gas produced any precipitate at all. When, however, the acid solution was first boiled with a little sodium hydrogen sulphite, the hydrogen sulphide immediately gave a precipitate.
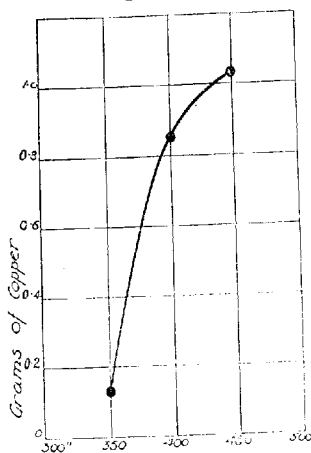
As the temperature rose, the colour of the fused sodium hydroxide deepened, and at 450° it had a distinctly brown tint. The number of shiny scales in the hydroxide increased considerably, and this probably accounts for the big increase in the percentage of copper in the alkali. No attempt was made to isolate any of the crystals, as they were invariably mixed with a red precipitate which accompanied the solution of the sodium hydroxide. They were also acted on by water, and after remaining for a short while were decomposed.

Fig. 5.

At 500° an interesting change was observed. The sodium hydroxide was very dark brown, and a large quantity of crystalline matter was found in the bottom of the crucible. The crystals were long and narrow, and quite different in shape and appearance from the scales observed at lower temperatures. At 550° still more of these crystals were formed. It was possible to pour off the sodium hydroxide and leave the crystals in the crucibles. They were removed, rapidly washed, and dried. In this way an impure sample was obtained, from which some large crystals were picked out.

The sodium hydroxide obtained at these high temperatures is very pretty when cooling in the mould, and finally gives a crystalline solid totally different in crystalline character from ordinary sodium hydroxide.

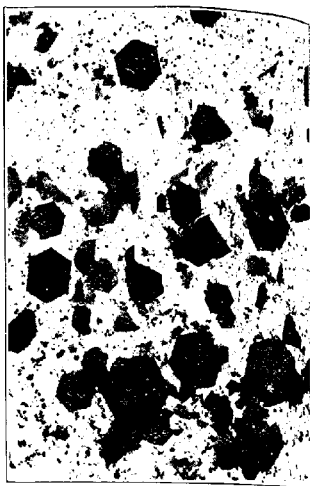At the lower temperatures the total percentage of copper in the

PLATE 1. × 30.

PLATE 2. × 30.

PLATE 3. × 30.
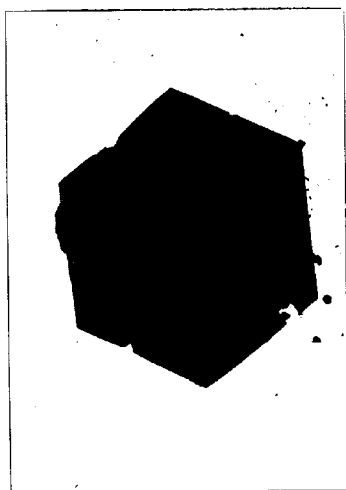
PLATE 4. × 30.
Reflected light.

sodium hydroxide was 0·067 at 350°, 0·440 at 400°, and 0·536 at 450°. Since the scales were always found in suspension, the above figures do not represent the exact amount of copper dissolved in the sodium hydroxide, but they give some idea of the relative amounts of copper dissolved from the crucible. The data, shown graphically in Fig. 5, refer to 200 grams of sodium hydroxide heated for four hours.

As there was not sufficient picked material, the analysis of the crystals was made on the impure sample. It consisted of a mixture of very small crystals and a little amorphous copper oxide. The sample was dissolved in hydrochloric acid, the copper precipitated in the usual way, the filtrate evaporated to dryness, and the residue dissolved and titrated with standard silver nitrate. The precipitate of copper sulphide was redissolved, and the copper estimated electrolytically.

The following are the analytical data :

Weight of sample	1·1131	grams.
„ of copper found	0·8716	gram.
„ of sodium in the filtrate	0·00591	„

It is reasonable to assume that such a small amount of sodium must be present as an impurity—probably due to incomplete washing, in which case it would be present as sodium carbonate. The weight of carbonate present would be 0·0131 gram. On this assumption, the actual weight of the crystals was $1·1131 - 0·0131 = 1·100$ grams. The percentage of copper in the crystals was therefore 79·2. This gives a final proportion of $Cu : O = 1·247 : 1·3 = 1 : 1·04$. From this it would seem that the crystals are a crystalline oxide of copper of the empirical formula CuO.

When examined with transmitted light, the crystals are quite opaque. From the photograph (Plate 1, magnification 30 diameters) it is seen that they are long, needle-shaped crystals which have, in unbroken specimens, truncated ends.

Conclusions.

(1) Compared with iron and nickel, copper can be said to be readily attacked and dissolved by fused sodium hydroxide.

(2) The actual amounts are still quite small—the highest being in the sodium hydroxide heated at 450°, which contains approximately 0·8 per cent. of copper, but it will be seen that the actual quantities are much greater than in the case of either iron or nickel. Since copper is much more easily oxidised than the other two metals, this supports the view that all these reactions of fused sodium hydroxide with metals commence with the oxidation of the metal.

(3) Crystals are obtained in the sodium hydroxide at all tem-

peratures.   At 350° to 500°, shiny scales are observed in the hydroxide.   Above 500°, the scales disappear and long, thin crystals are seen floating in the liquid.

(4) These long crystals are readily soluble in acids, are decomposed by water after a while, and are quite different in character from the crystals obtained with iron and nickel.   Their empirical formula is CuO.

C.—Action of Mixtures of Sodium Hydroxide and Sodium Peroxide on Metals.

1. Action with Iron.

In the previous section of this paper, reference was made to two kinds of crystals (yellow and red) produced by the action of sodium hydroxide on iron at temperatures above 550°.   The second attempt to prepare any quantity of these, was, for some unknown reason, unsuccessful.   It was thought that these crystals were the product of some oxidation process, and the lack of success in their preparation seemed to indicate the necessity for some stronger oxidising agent.   To achieve this, it was decided to add sodium peroxide. A preliminary experiment was carried out in one of the crucibles used previously.   A mixture of sodium hydroxide and 5 per cent. of sodium peroxide was heated in an iron crucible at 500 to 550° for four to eight hours.   The crucible and contents were then allowed to cool very slowly in the furnace.   When the sodium hydroxide was quite cold, it was found that a large quantity of red crystals had been formed.   The crystals were found adhering to the crucible and the surface of the sodium hydroxide, and they were much larger and better formed than any obtained previously. The hydroxide was broken up, but no sign of the yellow crystals was seen.   As the addition of sodium peroxide seemed to give a very promising result, a complete series of experiments was carried out at various temperatures.   Unless otherwise stated, the sodium hydroxide in the following experiments always contained 5 per cent. of sodium peroxide.

Results obtained.

Temp.	Description of the sodium hydroxide.	Particulars of crystals observed.	Percentage of iron in the solution.
350°	Greenish-blue.	Quantity of very small crystals.	0·024
	Free from suspended matter.	Mixed with the red oxide.	
400	Free from suspended matter.	Mixed with the red oxide.	0·025
450	Very black; gave a yellow ppte. on cooling.	Large quantity of red crystals in suspension.	0·11

Results obtained at 500—550°.

On one occasion a clear, dark green sodium hydroxide was formed which gave no yellow precipitate on cooling and in which there were no crystals of any kind. It contained 0·029 per cent. of iron in solution. This was quite evidently one of the exceptional cases which were met with every now and then.

The general results of heating sodium hydroxide with 5 per cent. of sodium peroxide in an iron crucible to 550° and leaving to cool slowly after about five hours' heating, were as follows :

(1) A large quantity of red crystals was formed.

(2) The sodium hydroxide was a dark, almost black, quite soft solid which dissolved in water very readily, usually with evolution of gas. The solution was deep purple, which rapidly became deep green, a large quantity of ferric oxide being precipitated. The green solution seemed permanent when very concentrated.

(3) When the sodium hydroxide was dissolved in a minimum quantity of water and the concentrated solution poured off after the insoluble matter had been allowed to settle, a mixture of substances was found in the sediment. In this, which was principally ferric oxide, there were a few red crystals and two substances different in appearance from anything we had seen previously. The separation of the latter substances was not attempted on any scale, but a few specimens were picked out and examined microscopically. Of the two new substances, one was in the form of long, narrow, blood-red crystals (almost opaque) with peculiar truncated ends, which were rapidly decomposed by water and deliquesced in the air. The other, of which there was a moderate quantity, consisted of small, flat pieces of rust-coloured matter. It was difficult to tell whether these were crystalline or not. They generally had a peculiar red sheen with reflected light.

An excellent sample of the red crystals was obtained by carefully cutting off the masses of crystals which had collected at the edge of the solid sodium hydroxide and dissolving in water. The crystals were so thick that they could be detached with very little adhering sodium hydroxide.

Results at Higher Temperatures.

Two iron crucibles containing sodium hydroxide with 5 per cent. and 10 per cent. of peroxide respectively were heated at 720° and allowed to cool very slowly in the furnace.

The hydroxide containing 5 per cent. of peroxide set to a green solid. On dissolving in water, a large quantity of the long, red

crystals with truncated ends was observed along with a small quantity of red crystals.

The hydroxide with 10 per cent. of peroxide set to a dark purple solid, and red crystals had been deposited in considerable quantity on the sides of the crucible. A large quantity of the long crystals and a small quantity of the red variety were seen when the sodium hydroxide was dissolved. It is seen from this that the long crystals are the product of reactions carried out at the higher temperatures.

Results obtained with the Use of Pure Sodium Peroxide.

It was found that the employment of larger quantities of sodium peroxide than those used, resulted in the crucibles being attacked very vigorously. Ordinary laboratory crucibles were usually eaten right through. In addition to this, it was found that as the amount of peroxide used was increased, the amount of crystals of all kinds diminished until with large amounts, such as 50 per cent., no crystals were found at all.

A thick cast-iron crucible containing sodium peroxide only was heated at 500—550° for about four hours, and left to cool in the usual way. The final product was a mass of long, very dark crystals which dissolved in water very readily, yielding a deep purple solution which deposited ferric oxide and turned green on keeping. These crystals were probably pure sodium ferrate.

Properties of the Red Crystals formed at 500°.

1. When examined under the microscope, it was seen that the crystals tended to be very perfect hexagons. All the available evidence, microscopic as well as chemical, showed that the yellow crystals and the red crystals are both modifications of one substance. The crystals are transparent and of a reddish-brown colour, the intensity varying with the thickness of the crystal. They have a refractive index slightly greater than that of oil of cinnamon ($n = 1.58$). Most of the crystals are lamellar and are really basal cleavage plates of hexagonal crystals which have a very perfect basal cleavage. With convergent light they readily give optical figures which show that the crystals are uniaxial and optically negative. A microphotograph (Plate 2, magnification 30 diameters) is given, in which the crystals, being red, appear quite black, and which shows the regular hexagon shape of the untouched crystals.

2. They are unacted upon by boiling water, boiling sodium hydroxide solution, and cold dilute mineral acids.

3. They are readily dissolved by hot concentrated acids.

4. They are stable up to at least 720° in fused sodium hydroxide.

5. They consist of sodium, iron, and oxygen. In view of this composition their stability is remarkable.

Analysis.

A known weight of the crystals was washed with water and the amount of Na_2O in the washings estimated.

The washed crystals were dissolved in hydrochloric acid, and the solution was carefully evaporated to dryness in either a platinum or porcelain dish. The residue was then gently heated until a constant weight was obtained, indicating that all the ferric chloride had been converted into oxide. The final residue was boiled with water, and the sodium chloride in the resulting liquor estimated by titration with silver nitrate. The sodium oxide estimated in the washings was assumed to be carbonate, and allowance was made for this in calculating the results. The solution of the crystals in acid was made up to 250 c.c. and 50 c.c. taken for each sodium estimation. The sodium figures for various estimations on the same solution agreed fairly well, showing that the method was satisfactory. The analysis of the crystals was never satisfactory.

The following are the average results of an analysis made immediately after the crystals were isolated : Fe $= 52·2$; Na $= 14·55$; O $= 30·25$ per cent.

Analyses made on a washed sample twelve months after its formation gave an iron content larger than the above by approximately 6 per cent.

It seems fairly definite that the crystals are composed of a mixture of oxides of sodium and iron, the latter probably functioning in an acidic capacity. The variations in the analyses are most likely due to the crystals themselves undergoing slow decomposition, which would of course introduce differences. This is shown by the fact that no matter how carefully the crystals are washed, if they be kept for any length of time and then rewashed, the washings will always contain a further quantity of sodium. No weight can therefore be put on the analysis for the purpose of obtaining a molecular formula, but it seems possible that immediately after the removal they have a composition represented by the formula $Na_2Fe_3O_6$.

2. *Action with Nickel.*

A series of experiments similar to those with iron crucibles were carried out with nickel. These experiments were made at the

TABLE III.

Results with Nickel and Sodium Hydroxide containing Sodium Peroxide.

Temp.	Sodium peroxide per cent.	Colour of fused sod³ m hydroxide.	Condition.	Cooling phenomena.	Suspended matter.	Porcentage of nickel in the sodium hydroxide.
350°	5	Dark green.	Clear, with slight scum.	Black ppte. on cooling.	None.	0·0024
400	,,	Brown.	Clear.	Large black ppte. and vigorous bubbling on cooling.	Large quantity of silvery crystals.	0·0135
450	,,	,,	,,	,, ,, ,, ,,	,, ,, ,, ,,	
500	,,	,,	,,	Large black ppte., but no bubbling.	Larger quantity of crystals.	0·0131
720	,,	Allowed to cool slowly in the furnace.			Few crystals on the surface. None in the mass of the sodium hydroxide.	
	10	Grey solid. Allowed to cool slowly in the furnace. Shiny black mass of sodium hydroxide and silvery crystals, more like graphite than sodium hydroxide. Apart from the crystals, the hydroxide had crystallised in a kind of check pattern, totally different from anything seen before.				

same time as the second series of experiments with sodium hydroxide and nickel, the crucibles all being in the furnace together. The principal aim was to ascertain if the silvery crystals observed on one occasion in the first series would be produced in any quantity by the addition of sodium peroxide to the hydroxide.

From Table III it is seen that this object was accomplished, and from the mass of silvery crystals obtained at 720° a large sample was prepared.

These crystals were much more easily separated than the corresponding iron ones, as there was practically no precipitate when the sodium hydroxide dissolved in water, and nothing analogous to the red oxide. A little nickel oxide was present, but this was easily got rid of by swirling the solution and decanting the liquor containing the bulk of the crystals. There were no signs of any other crystalline substances.

Examination of the Crystals.

(1) When examined under the microscope with transmitted light, these crystals are quite opaque. They are, however, very similar in form to the crystals obtained with iron crucibles, that is, they crystallise in regular hexagons, as is shown from a single crystal on Plate 3. If, however, they are examined with reflected light, it is seen that the crystals are regularly etched. Frequently the etching is seen as parallel bands, very similar in appearance to the parallel twin bands of plagioclase. At times, however, more or less complete equilateral triangles are seen (Plate 4), which shows that the crystals have symmetry of the hexagonal system.

(2) The crystals are stable in fused sodium hydroxide up to 50° and are unacted on by water and cold dilute acids.

(3) They are readily dissolved by hot concentrated acids, and berate chlorine from hydrochloric acid.

(4) They consist of nickel, sodium, and oxygen.

Analysis.

This analysis was again unsatisfactory, but an average analysis gives $Ni = 53.6$; $Na = 8.4$; $O = 38.0$ per cent.

The sodium was estimated in the manner described for the iron compound. The nickel chloride was very readily reduced to the oxide. The percentage obtained was the average of several results obtained on four lots of the solution, namely, 8.38, 8.7, 8.5, 8.46. The nickel was estimated by the glyoxime method, and the oxygen by difference. The average analysis indicates an empirical formula

TABLE IV.

Results with Copper and Sodium Hydroxide containing Sodium Peroxide.

Temp.	Sodium peroxide per cent.	Description of the sodium hydroxide.	Behaviour with water.	Crystals observed.	Percentage of copper in the solution.
350°	5	Dark brown and clear.	Dissolved readily with evolution of gas, giving clear, colourless solution.	None.	Trace.
400	,,	,, ,, ,, ,,	,, ,, ,,	,,	0·013
450	,,	,, ,, ,, ,,	Pale blue solution.	,,	0·08
500	,,	,, ,, ,, ,,	,, ,, ,,	Large quantity of brown, shiny scales similar to those obtained with sodium hydroxide alone at 350–500°.	
550	,,	,, ,, ,, ,,	,, ,, ,,	A few long crystals in suspension.	0·05
350	10	Greyish solid with the "check" crystalline appearance previously noted.	Clear blue solution.	None.	
400	,,	Black solid.		A few crystals adhering to the crucible.	0·14
450	,,	"Check" crystalline appearance very pronounced.			

3s

of $Na_2Ni_5O_{13}$. It was found that the crystals were unstable over long periods of time and in this respect were similar to the iron crystals already described. When crystals which had been very thoroughly washed with water were kept for a period of, say, a week, sodium compounds were always found in the washings when they were rewashed. This will account for the unsatisfactory analysis.

3. *Action with Copper.*

A parallel series of experiments to those described with copper and sodium hydroxide was carried out in similar crucibles with lium hydroxide and 5 per cent. of sodium peroxide. A few ditional experiments with 10 per cent. of peroxide were performed. The results obtained (see Table IV) were quite unexpected, being the reverse of those obtained with iron and nickel. There, the tion on the metal was much increased by the addition of peroxide, hilst with copper the action was considerably reduced.

Conclusion.

So far as the formation of crystalline substances and the removal copper from the crucibles are concerned, the addition of the roxide seemed to have a prohibiting effect, in marked contrast that produced by peroxide with iron or nickel crucibles.

Summary.

The chemical properties of fused sodium hydroxide have been died in three respects.

(1) *The Water Content.*

By fusing sodium hydroxide in a vacuum, it has been found at it has an average water content of 1·1 per cent. In connexion th these experiments, it is evident that the presence of oxygen necessary before the fused hydroxide becomes coloured in its al manner. In a vacuum, the iron of the containing vessel is e to act as a reducing agent on the small quantities of impurities the hydroxide.

(2) *Action on iron, nickel, and copper in air.*

a) These reactions have been studied between 350° and 600°.
b) In no case is the amount of metal dissolved in the sodium roxide very high. The maximum amount, which was obtained copper, was 0·73 per cent.
c) Iron is less vigorously attacked than copper, and more rously than nickel.

(d) The formation of crystalline substances by the action of fused sodium hydroxide on each of these metals has been noted and their separation described.

(3) *Action of iron, nickel, and copper with sodium hydroxide containing 5 per cent. of sodium peroxide.*

(a) This action has been studied at temperatures ranging from 350° to 720°.

(b) The formation of crystalline substances previously noted is found to be facilitated in the case of iron and nickel at certain temperatures between 500° and 700°. The substances formed in the largest quantities have been described and analysed. In the case of copper, the formation of crystals is retarded.

(c) The reaction between sodium hydroxide, sodium peroxide, and iron or nickel is almost certain to have a parallel with similar metals such as cobalt, chromium, or manganese, and it is extremely probable that research with other metals on the lines indicated would reveal the presence of new crystalline substances, similar to those we have described.

CCXI.—*Some Derivatives of Monothioethylene Glycol.*

By GEORGE MACDONALD BENNETT and EDITH MURIEL WHINCOP.

THE preparation of monothioethylene glycol was recently described (this vol., p. 423) and we have now prepared a few crystalline derivatives of this interesting and reactive substance. As one of us is obliged to withdraw from the work, it seems best to publish the results which have so far been obtained.

Owing to the tendency of the mercaptan to become oxidised in alkaline solution, a Schotten-Baumann reaction led to the corresponding acylated disulphide. Mercaptans have been shown (Goldschmidt and Meissler, *Ber.*, 1890, **23**, 272) to react with phenylcarbimide in a manner analogous to the reaction with alcohols; with monothioethylene glycol, the molecule of which contains both a thiol and a hydroxyl group, phenylcarbimide reacted at once,

addition taking place, as was perhaps to be expected, preferentially at the thiol group, and a substance was produced of the formula $C_6H_5 \cdot NH \cdot CO \cdot S \cdot C_2H_4 \cdot OH$.

It was hoped that the series of compounds $S(C_2H_4 \cdot OH)_2$, $C_2H_4(S \cdot C_2H_4 \cdot OH)_2$, $S(C_2H_4 \cdot S \cdot C_2H_4 \cdot OH)_2$, etc., might be extended by successive condensation of the corresponding halogen compounds with monothioethylene glycol. An examination of the higher members of this series, or of the unsaturated substances derived from them, which evidently approximate more and more closely in composition to diethylene disulphide, might throw light on the nature of the amorphous products of high molecular weight obtained from the interaction of ethylene dibromide and alkali sulphides by Crafts (*Annalen*, 1862, **124**, 110; 1863, **128**, 220), V. Meyer (*Ber.*, 1886, **19**, 3262) and Mansfield (*ibid.*, 1886, **19**, 697). The series was not, however, carried beyond the third member, for the dichloro-compound derived from this seems to be much more unstable than its lower homologues, and could not be isolated. Ethylene *bis*-β-chloroethyl sulphide,

$$CH_2Cl \cdot CH_2 \cdot S \cdot CH_2 \cdot CH_2 \cdot S \cdot CH_2 \cdot CH_2Cl,$$
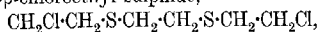
has the very reactive chlorine common with β-chloro-sulphides, and its physiological action is very noticeable. In marked contrast to this is the low reactivity of the halogen in the β-halogenated 2 : 4-dinitrophenyl ethyl sulphides.

EXPERIMENTAL.

β-*Hydroxyethyl phenylthiocarbamate*, $C_6H_5 \cdot NH \cdot CO \cdot S \cdot C_2H_4 \cdot OH$, was produced when molecular proportions of phenylcarbimide and monothioethylene glycol were warmed together for a few seconds. It is a cream-coloured solid of m. p. 59—60°, which crystallises well from benzene or carbon tetrachloride (Found : $N = 7 \cdot 19$; $S = 16 \cdot 0$. $C_9H_{11}O_2NS$ requires $N = 7 \cdot 11$; $S = 16 \cdot 25$ per cent.). It is easily soluble in these solvents or in alcohol, but insoluble in light petroleum or water. It shows none of the reactions of a mercaptan, giving no mercury compound when its alcoholic solution is boiled with mercuric oxide, and having no reducing action on ferric chloride.

ββ′-*Di*-p-*nitrobenzoyloxydiethyl disulphide*,

$$(NO_2 \cdot C_6H_4 \cdot CO \cdot O \cdot CH_2 \cdot CH_2)_2S_2,$$
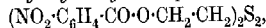
was the main product when monothioethylene glycol was treated with p-nitrobenzoyl chloride in presence of aqueous sodium hydroxide. It crystallised in pale buff-coloured plates from butyl alcohol or methyl acetate, m. p. 145° (Found : $N = 6 \cdot 1$; $M = 353$. $C_{18}H_{16}O_8N_2S_2$ requires $N = 6 \cdot 2$ per cent.; $M = 452$). The product from the above reaction contained also a substance of lower melting

point, which was continually oxidised during purification with production of the disulphide.

An *additive* compound, C_2H_6OS,C_2HOCl_3, was formed with evolution of heat when the mercaptan was mixed with chloral in benzene solution. It crystallised in colourless needles on addition of light petroleum, and melted rather indefinitely at 67—68°. The substance was very deliquescent and too unstable to purify (Found: Cl = 50·7, 51·2. $C_4H_7O_2Cl_3S$ requires Cl = 47·2 per cent.).

*Ethylene* bis-β-*Hydroxyethyl Sulphide,*

$$HO\cdot CH_2\cdot CH_2\cdot S\cdot CH_2\cdot CH_2\cdot S\cdot CH_2\cdot CH_2\cdot OH.$$
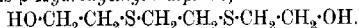
—Ethylene dibromide (12 grams) was cautiously added to a solution prepared from sodium (3 grams) and the monothioglycol (10·5 grams) in rectified spirit (60 c.c.). The solution became neutral to litmus after boiling for fifteen minutes; the sodium bromide was removed by filtration and the filtrate evaporated. The crude product (obtained in quantitative yield) was purified by recrystallisation from methyl acetate or ethyl ether, from which it separated in colourless plates melting sharply at 64° (Found : C = 39·2; H = 7·67. $C_6H_{14}O_2S_2$ requires C = 39·5; H = 7·70 per cent.).

This substance is readily soluble in water, alcohol, or hot methyl acetate, less so in benzene or light petroleum. Its solution in alcohol (and that of the corresponding trisulphide described below) dissolves a considerable quantity of sodium chloride. It is stable to heat, distilling undecomposed at atmospheric pressure. Considerable difficulty was found in analysing it, an unusual length of combustion tube being necessary to ensure complete oxidation. A crystalline methiodide could not be obtained. When the substance was heated with boiling concentrated hydrochloric acid, it dissolved, and an oil separated which solidified in the cold. This was crystallised from light petroleum, but was apparently a mixture, its low chlorine content showing that any dichloro-compound produced had partly decomposed—probably with production of the corresponding unsaturated compound.

Ethylene bis-β-*Chloroethyl Sulphide,*

$$CH_2Cl\cdot CH_2\cdot S\cdot CH_2\cdot CH_2\cdot S\cdot CH_2\cdot CH_2Cl.$$
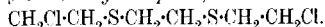
—The pure dihydroxy-compound described above was dissolved in an excess of purified thionyl chloride, and when the reaction was complete, the excess of the reagent was removed by heating on the water-bath under diminished pressure. The residue crystallised on cooling, and the colourless crystals were drained on porous earthenware in a desiccator over potassium hydroxide (Found: Cl = 30·4. $C_6H_{12}Cl_2S_2$ requires Cl = 32·4 per cent.). The compound melts at 54°. The reactivity of the chlorine is similar to that found with ββ'-dichlorodiethyl mono- and di-sulphides (com-

pare this vol., p. 424), and although no exact comparison has been made, the substance appears to have a distinctly stronger vesicant action than ββ'-dichlorodiethyl sulphide. When attempts were made to recrystallise it from light petroleum, it became partly decomposed or hydrolysed (Found : Cl = 12·7 per cent.).

Sulphido-bis-β-*hydroxydiethyl Sulphide,*

$$S(CH_2 \cdot CH_2 \cdot S \cdot CH_2 \cdot CH_2 \cdot OH)_2.$$

—ββ'-Dichlorodiethyl sulphide (5·3 grams) was added to a solution prepared from a slight excess over the calculated weights of mono-thioethylene glycol and sodium in rectified spirit (20 c.c.), and the reaction was completed by heating on the water-bath for a few minutes until the alkalinity had disappeared. The solution, separated by filtration from the sodium chloride which had been precipitated, deposited a white solid on cooling. This was purified by crystallisation from hot acetone or methyl acetate, in which it was readily soluble, and was thus obtained as colourless plates, m. p. 91—92° (Found : C = 39·2; H = 7·35. $C_8H_{18}O_2S_3$ requires C = 39·6; H = 7·45 per cent.). This substance is less readily soluble in water or alcohol than the disulphide described above. It resembles the latter in its behaviour when heated with concentrated hydrochloric acid. When attempts were made to convert it into the corresponding dichloro-compound by the action of thionyl chloride, as with the dihydroxy-disulphide, a sudden evolution of gas occurred on raising the temperature, owing to decomposition, and no definite compound was isolated.

A *diacetyl* derivative was obtained by acetylation with acetic anhydride and sodium acetate as a white solid, m. p. 51° after crystallisation from light petroleum (Found : C = 44·2; H = 6·69. $C_{12}H_{22}O_4S_3$ requires C = 44·2; H = 6·76 per cent.).

Condensation of Monothioethylene Glycol with Chloro-2 : 4-dinitrobenzene.

When chloro-2 : 4-dinitrobenzene was treated with a solution of the sodium salt of the monothioglycol (1 equivalent) in rectified spirit, the desired sulphide was produced in almost the calculated yield, provided that the solutions were mixed cold and the temperature of the mixture was not allowed to rise rapidly. Otherwise a violent reaction occurred, the solution became almost black, and a chocolate-brown solid subsequently crystallised, having m. p. 143°, which did not contain sulphur and was probably an azoxy-compound. When the reaction proceeded smoothly, the sodium chloride quickly separated as the temperature was gradually raised, and the reaction was completed by heating the solution

for a few minutes on the water-bath. The product was precipitated by pouring the solution into a large volume of water, and was recrystallised from benzene.

2 : 4-*Dinitrophenyl* β-*hydroxyethyl sulphide*,

$$C_6H_3(NO_2)_2 \cdot S \cdot CH_2 \cdot CH_2 \cdot OH,$$
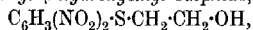
was thus obtained in bright yellow needles, m. p. 99—100° (Found: N = 11·6; S = 12·6. $C_8H_8O_5N_2S$ requires N = 11·5; S = 13·1 per cent.). The substance is readily soluble in alcohol, but sparingly so in cold benzene. It is decomposed when heated with concentrated aqueous potassium hydroxide, some diethylene disulphide being produced. It is unaffected by boiling concentrated hydrochloric acid or by thionyl chloride. Fusion with phosphorus pentachloride at once converts it into 2 : 4-*dinitrophenyl* β-*chloroethyl sulphide*, $C_6H_3(NO_2)_2 \cdot S \cdot CH_2 \cdot CH_2Cl$, which crystallises from methyl alcohol in rectangular plates of a deep yellow colour, m. p. 97° (Found : Cl = 13·6. $C_8H_7O_4N_2ClS$ requires Cl = 13·46 per cent.).*

This chloro-compound, when boiled for half an hour with a large excess of sodium ethoxide in alcoholic solution, did not yield the whole of its chlorine in the ionic condition. It does not combine with bromine in chloroform solution. When warmed for a few minutes with fuming nitric acid, it gave a *sulphoxide* which crystallised from methyl alcohol in brilliant yellow needles, m. p. 123° (Found : Cl = 12·15. $C_8H_7O_5N_2ClS$ requires Cl = 12·31 per cent.).

2 : 4-*Dinitrophenyl* β-*bromoethyl sulphide*, obtained from the corresponding hydroxy-compound by the action of phosphorus tribromide in benzene solution, crystallises from light petroleum in minute, lemon-yellow plates, m. p. 91—92° (Found : Br = 25·9. $C_8H_7O_4N_2BrS$ requires Br = 26·05 per cent.), and gives a *sulphoxide*, lemon-yellow needles from alcohol, m. p. 136° (Found : Br = 24·65. $C_8H_7O_5N_2BrS$ requires Br = 24·75 per cent.).

We wish to thank Messrs. Strange and Graham, Ltd., for the facilities which they have afforded us for this work.

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* In estimating halogens by the Robertson method (T., 1915, **107**, 904), the use of 2 grams of sodium perborate is to be recommended in place of 10 c.c. of hydrogen peroxide solution, as being more easily obtained free from chlorides.
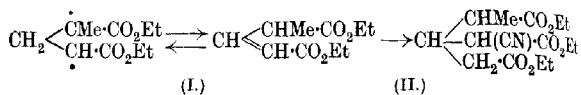
CCXII.—*Experiments on the Synthesis of the Polyacetic Acids of Methane. Part IV. Conditions of Formation by the Cyanoacetic Ester Method of Stable Methanetriacetic Esters.*
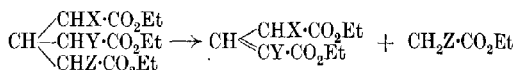
By Christopher Kelk Ingold and Edward Arthur Perren.

In Part I of this series (this vol., p. 341) attention has been directed to the difficulty which in many instances attends the conversion of the mobile glutaconic esters into derivatives of methanetriacetic acid by condensation with ethyl cyanoacetate, and is to be traced to the permanence of the "normal" forms of the glutaconic esters. One of the purposes of the present paper is to show that by suitably applying the knowledge gathered by Thorpe and his collaborators regarding the conditions controlling the relative stability of the normal and unsaturated forms of the glutaconic esters it is possible to obtain condensation products of the desired type.

It has been pointed out (*loc. cit.*; Ingold and Thorpe, this vol., p. 493) that equilibrium between and speed of interconversion of the two forms of a glutaconic acid derivative are fundamentally conditioned by substitution in the three-carbon system, and that the permanence of the normal modification is dependent on symmetry. α-Substitution, therefore, since it is unsymmetrical substitution, although it may not much affect dynamic mobility, always tends greatly to reduce the permanence of the normal form and to shift the equilibrium in the direction favouring the unsaturated isomeride, whilst β-substitution, although not seriously altering the static relation between the two forms at equilibrium, invariably effects a considerable reduction in the speed of interconversion. The conditions which most facilitate the condensation of an equilibrated glutaconic ester with ethyl cyanoacetate to form a derivative of methanetriacetic acid are (a) that the equilibrium should as far as possible favour the unsaturated modification, (b) that the ester should be sufficiently mobile to regenerate the unsaturated form as fast as the condensation process removes it. Hence, of all the simpler, equilibrated esters of the glutaconic series, α-methylglutaconic ester should be that which will most readily react with ethyl cyanoacetate to form a product of the methanetriacetic acid type. Actually this is the case; equilibrated α-methylglutaconic ester (I) condenses with ethyl sodio-
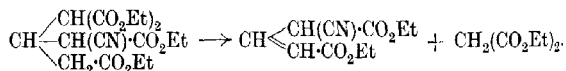
cyanoacetate to give ethyl ω-cyano-ω'-methylmethanetriacetate (II) in almost quantitative yield :

$$CH_2\begin{matrix}\diagup CMe\cdot CO_2Et\\ \diagdown CH\cdot CO_2Et\end{matrix}\xrightarrow{}\underset{\longleftarrow}{}CH\begin{matrix}\diagup CHMe\cdot CO_2Et\\ \diagdown CH\cdot CO_2Et\end{matrix}\longrightarrow CH\begin{matrix}\diagup CHMe\cdot CO_2Et\\ -CH(CN)\cdot CO_2Et\\ \diagdown CH_2\cdot CO_2Et\end{matrix}$$

(I.)   (II.)

In Part III (this vol., p. 1582) it was pointed out that of the comparatively few methanetriacetic esters which are capable of being *formed* from glutaconic esters by the cyanoacetic ester method a considerable proportion are unstable and decompose completely into smaller molecules under the conditions of their formation. The cause of these decompositions is the reversibility of the Michael reaction; the determining factors affecting particular cases are (largely, at any rate) spatial. Thus, certain methanetriacetic acid derivatives containing two or three branched acetic acid chains attached to the methane carbon atom decompose, as we have shown (*loc. cit.*), according to the equation

$$CH\begin{matrix}\diagup CHX\cdot CO_2Et\\ -CHY\cdot CO_2Et\\ \diagdown CHZ\cdot CO_2Et\end{matrix}\longrightarrow CH\begin{matrix}\diagup CHX\cdot CO_2Et\\ \diagdown CY\cdot CO_2Et\end{matrix}+CH_2Z\cdot CO_2Et$$

(a retrograde Michael condensation, therefore) to an extent apparently determined by the space occupied by the branched chains, and therefore by the volumes of the groups X, Y, Z. The greater the volumes of the adjacent residues, the greater is the tendency towards decomposition into smaller molecules. Now, although the exact conditions *necessary and sufficient* to determine this reaction can only be discovered by an extended research, it is apparent from the previous investigation that in methanetriacetic acid derivatives the existence of two branched acetic acid chains is a *necessary* circumstance. That, although necessary, it is not always *sufficient* is proved by the stability of the ester II. Yet, one must observe, if the methyl group in this ester be replaced by a large group, for example, carbethoxyl, decomposition will ensue (with elimination of ethyl malonate) :

$$CH\begin{matrix}\diagup CH(CO_2Et)_2\\ -CH(CN)\cdot CO_2Et\\ \diagdown CH_2\cdot CO_2Et\end{matrix}\longrightarrow CH\begin{matrix}\diagup CH(CN)\cdot CO_2Et\\ \diagdown CH\cdot CO_2Et\end{matrix}+CH_2(CO_2Et)_2.$$

Moreover, the difference of stability is not due to the impossibility of eliminating a residue, such as ·CHMe·CO$_2$Et, as an ester (ethyl propionate) which cannot take part to any appreciable degree in a direct Michael condensation; for the residue in question will be

readily extruded if a substituent be introduced into the third acetic acid chain (*loc. cit.*) :

$$CH{\Large\langle}\begin{array}{l}CHMe \cdot CO_2Et \\ CH(CN) \cdot CO_2Et \\ CH(CN) \cdot CO_2Et\end{array} \longrightarrow CH{\Large\langle}\begin{array}{l}CH(CN) \cdot CO_2Et \\ C(CN) \cdot CO_2Et\end{array} + CH_2Me \cdot CO_2Et.$$
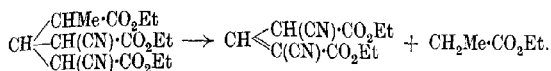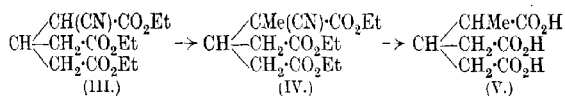
The ester II, therefore, is one of the few amongst its analogues so constituted that in its preparation one escapes both the inhibiting circumstances ordinarily met with. On complete hydrolysis it yields ω-methylmethanetriacetic acid (V), which may therefore be prepared in quantity by this method; it has already been obtained by Skraup (*Monatsh.*, 1900, **21**, 910) by the degradation of quinine *via* cincholeuponic acid. Skraup also obtained the acid, in sufficient quantity to identify it with the substance derived from quinine, by hydrolysing the crude condensation product of α-methylglut-aconic and malonic esters, but in view of the capacity possessed by glutaconic derivatives for yielding products of 1 : 3-addition, no synthesis of this kind can be regarded as a proof of structure. We have, however, definitely established the constitution of the acid, and therefore that of the ester (II), by proving the identity of the acid with that obtained by hydrolysing the ester (IV). This ester is prepared by methylating ethyl ω-cyanomethanetriacetate (III) (compare this vol., p. 352), and its constitution is not open to question.

$$CH{\Large\langle}\begin{array}{l}CH(CN) \cdot CO_2Et \\ CH_2 \cdot CO_2Et \\ CH_2 \cdot CO_2Et\end{array} \rightarrow CH{\Large\langle}\begin{array}{l}CMe(CN) \cdot CO_2Et \\ CH_2 \cdot CO_2Et \\ CH_2 \cdot CO_2Et\end{array} \rightarrow CH{\Large\langle}\begin{array}{l}CHMe \cdot CO_2H \\ CH_2 \cdot CO_2H \\ CH_2 \cdot CO_2H\end{array}$$
$$\qquad\qquad(III.)\qquad\qquad\qquad (IV.)\qquad\qquad\qquad (V.)$$

With this communication it is proposed to close for the present our examination of the conditions governing the synthesis of the methanepolyacetic acids by the cyanoacetic ester method; to turn on the one hand to other methods of producing these acids, and on the other to what appear to be the logical consequences regarding the circumstances controlling carbon-chain formation in general, of the clues which the investigation has afforded.

EXPERIMENTAL.

Condensation of Ethyl α-Methylglutaconate with Ethyl Cyanoacetate.

Ethyl α-methylglutaconate (9 grams) was added to a suspension in ethyl alcohol of ethyl sodiocyanoacetate prepared by dissolving 1 gram of sodium in 20 grams of ethyl alcohol and adding 5 grams of ethyl cyanoacetate. When the mixture was heated on the

3 s*

steam-bath, the ethyl sodiocyanoacetate rapidly dissolved and another sodium compound separated from the brown solution. After twenty-four hours, water was added, and the products were extracted by means of ether after acidification with hydrochloric acid.

Ethyl ω-Cyano-ω'-methylmethanetriacetate (II).

The extracted esters were separated into neutral and acid portions by washing the ethereal extract with sodium carbonate solution in the usual manner, and the neutral fraction was distilled under diminished pressure. The ester was thus obtained as a colourless oil, b. p. 218—222°/22 mm. The yield was 11 grams, and a further quantity was obtained by esterifying the acid condensation product by means of ethyl alcohol (Found : C = 57·2; H = 7·3. $C_{15}H_{23}O_6N$ requires C = 57·5; H = 7·3 per cent.).

ω-Methylmethanetriacetic Acid (V).

The ester was mixed with an equal volume of cold concentrated sulphuric acid, and, after keeping for one hour, with a similar amount of water. The whole was boiled until carbon dioxide ceased to be expelled, more water was then added, and the boiling was continued for five hours, the condenser being removed from time to time to facilitate the escape of ethyl alcohol. The product of hydrolysis was extracted by pure ether, and was recovered by evaporating the solvent as a colourless syrup, which, on touching with a glass rod, immediately set to a cake of crystals with evolution of heat. It separated from ethyl acetate in prisms, m. p. 138—139° (Found : C = 47·1; H = 6·1. Calc., C = 47·1; H = 5·9 per cent.). Its identity with the acid obtained (this vol., p. 1600) by hydrolysing the methylation product of ethyl ω-cyanomethane-triacetate was conclusively established by directly comparing the two substances and by a mixed-melting point determination.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
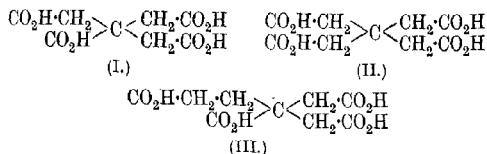   SOUTH KENSINGTON, S.W.7.   [Received, September 23rd, 1921.]

CCXIII.—*Experiments on the Synthesis of the Polyacetic Acids of Methane. Part V. The Preparation of Carboxymethanetriacetic Acid.*

By CHRISTOPHER KELK INGOLD and WALTER JAMES POWELL.

THE synthesis of the methanepolyacetic acids by the cyanoacetic ester method, although it has been successful in certain directions, is controlled by circumstances which effectively prevent the preparation of some of the desired substances. It has therefore become necessary to discover other methods of synthesis.

Since the methanepolyacetic acids are required for the preparation of associated alicyclic compounds, the number of methods available is necessarily restricted; when large amounts are needed, the method of production should be both rapid and inexpensive.

*cyclo*Hexane-1 : 1-diacetic acid, the preparation of which in quantity from *cyclo*hexanone and ethyl cyanoacetate has been standardised in this laboratory, on oxidation under conditions which bring about the fission of the *cyclo*hexane ring, might give the C_8-acid (I) and one or both of the two possible C_9-acids (II) and (III) :

$$\begin{matrix} CO_2H\cdot CH_2 \\ CO_2H \end{matrix}\!\!>\!\!C\!\!<\!\!\begin{matrix} CH_2\cdot CO_2H \\ CH_2\cdot CO_2H \end{matrix} \qquad \begin{matrix} CO_2H\cdot CH_2 \\ CO_2H\cdot CH_2 \end{matrix}\!\!>\!\!C\!\!<\!\!\begin{matrix} CH_2\cdot CO_2H \\ CH_2\cdot CO_2H \end{matrix}$$

$$\text{(I.)} \qquad\qquad\qquad\qquad \text{(II.)}$$

$$\begin{matrix} CO_2H\cdot CH_2\cdot CH_2 \\ CO_2H \end{matrix}\!\!>\!\!C\!\!<\!\!\begin{matrix} CH_2\cdot CO_2H \\ CH_2\cdot CO_2H \end{matrix}$$

$$\text{(III.)}$$

Carboxymethanetriacetic acid (I), and methanetetra-acetic acid (II), the preparation of which formed part of the original program of the research (this vol., p. 341), have not yet been obtained, and it would appear that, provided the correct experimental conditions can be found, the oxidation of *cyclo*hexane-1 : 1-diacetic acid should afford an extremely simple and direct method for the production of these substances.

Our experiments have been concerned mainly with the action of hot alkaline permanganate on *cyclo*hexane-1 : 1-diacetic acid, and we have succeeded in producing by this means an acid of the formula $C_9H_{12}O_8$. Unfortunately, however, we have been unable to determine which of the two possible formulæ (II and III) expresses its constitution, for the reason that the conditions of its formation appear to lie between extremely narrow limits, and we have not yet discovered how to standardise them sufficiently to enable a

satisfactory quantity of the substance to be prepared. On the other hand, we have found that by employing more concentrated permanganate it is possible to obtain an excellent yield of a tetrabasic acid, $C_8H_{10}O_8$, which can only be the required carboxymethanetriacetic acid (I).

It is fortunate that the handling of bulky solutions, unavoidable in carrying out permanganate oxidations with even moderately arge quantities of material, does not constitute a difficulty in the preparation of carboxymethanetriacetic acid by this method; for in the large-scale laboratory recently erected in this College the manipulation of considerable volumes has become an easy matter. The method, therefore, appears to satisfy all the conditions imposed by the object with which it was elaborated.

Carboxymethanetriacetic acid (I) may also be obtained by oxidising *cyclo*pentane-1 : 1-diacetic acid :

$$\begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix} > C < \begin{matrix} CH_2 \cdot CO_2H \\ CH_2 \cdot CO_2H \end{matrix} \longrightarrow \begin{matrix} CO_2H \cdot CH_2 \\ CO_2H \end{matrix} > C < \begin{matrix} CH_2 \cdot CO_2H \\ CH_2 \cdot CO_2H \end{matrix}$$

but an acid $C_9H_{12}O_8$ could not be isolated from the product.

EXPERIMENTAL.

(A) *Oxidation of* cyclo*Hexane-*1 : 1-*diacetic Acid.*

A considerable number of experiments have been carried out with a view to obtain information regarding the effect of experimental conditions on the decomposition of *cyclo*hexane-1 : 1-diacetic acid by alkaline permanganate, the variable factors the influence of which has been studied being (*a*) initial concentration of permanganate, (*b*) excess quantity of permanganate, (*c*) temperature, (*d*) time. The experiments were conducted in thermostats and the conditions controlled with all possible care. In this way it was shown that :

(i) within the range covered by the experiments, the two acids described below are the only two substances produced besides carbon dioxide and water.

(ii) by correctly regulating the conditions, carboxymethane-triacetic acid becomes the sole crystalline product.

The Acid $C_9H_{12}O_8$ (II or III).

This acid was isolated from the products of experiments in which a 50 per cent. excess of 3 per cent. potassium permanganate was employed, the temperature being that of the steam-bath and the time allowed fifteen hours. We are unable to make a precise statement of the conditions most favourable to its production, since

the yield, although sometimes amounting to 30 per cent. of the theoretical, was extremely variable and appeared to be influenced by some circumstance other than those which we sought to control. The acid was isolated from the solution in the way described in connexion with the preparation of carboxymethanetriacetic acid (below), and was separated from the unchanged *cyclo*hexane-1 : 1-diacetic acid, which always accompanied it, by triturating with cold water (in which the diacetic acid is almost insoluble). It was purified by crystallisation from a mixture of chloroform and ether, from which it separated in dense prisms, m. p. 120° (decomp.) (Found : C = 43·3; H = 5·2. $C_9H_{12}O_8$ requires C = 43·5; H = 4·9 per cent.).

The acid cannot be titrated satisfactorily and in this respect it resembles the carboxymethanetriacetic acid described below; indeed, this appears to be a property of many polybasic aliphatic acids and especially of those which readily form anhydrides. However, the results obtained clearly indicated that the acid was tetrabasic. The acid also resembles carboxymethanetriacetic acid in its extreme solubility in water, its capacity for separating with water of crystallisation, and in the insolubility of its barium salt; there can, we think, be no doubt that the two substances have closely analogous constitutions.

Carboxymethanetriacetic Acid (I).

Carboxymethanetriacetic acid is always formed to some extent when *cyclo*hexane-1 : 1-diacetic acid is oxidised by alkaline permanganate. The limits of successful experiment, however, are not widely separated, as under mild conditions, for example, those made use of in the preparation of the acid $C_9H_{12}O_8$ (above), a considerable quantity of *cyclo*hexanediacetic acid is usually left unattacked, whilst if the conditions be too drastic, for instance, if a 150 per cent. excess of 7 per cent. permanganate be employed at 103° for twenty-four hours, a large proportion of the material will be converted into carbon dioxide and water. The crystalline product in these circumstances consists solely of carboxymethanetriacetic acid, but the yield is correspondingly poor. The following conditions are the best that we have so far found for the preparation of carboxymethanetriacetic acid in quantity.

1·5 Kilograms of potassium permanganate were dissolved in 25 litres of water at 80° contained in a steam-heated, enamelled iron pan, and 106 grams of sodium carbonate followed by 200 grams of *cyclo*hexanediacetic acid were gradually added. The total volume was then made up to 30 litres by the addition of hot water, and the

supply of steam entering the jacket of the pan was so regulated that the temperature remained at 80° for ten hours while the solution was continuously stirred in order to prevent the manganese dioxide collecting on the sides and bottom of the pan and disturbing the temperature equilibrium. The steam supply was turned off over-night, but on the next day the stirring and heating were recommenced, and the temperature of the solution was again maintained at 80° for ten hours. On the third day, the cooled solution was acidified by adding 1·5 litres of concentrated hydrochloric acid, and was then treated with a stream of sulphur dioxide until the excess of permanganate had been reduced and the manganese oxides completely dissolved. The clear solution was concentrated to a small bulk, cooled, and filtered. The solid portion was washed with cold water and dried in a vacuum at 100°, but it was found to contain no appreciable quantity of organic matter. The filtrate was evaporated completely, and the residue dried in vacuum-ovens, ground in a mill, and extracted with hot acetone, from which, on evaporation, the acid was obtained as a syrup which gradually set to a hard, crystalline cake. The yield of crude acid was 165 grams (70 per cent. of the theoretical). It is not decreased by a considerable increase in the scale of the experiment.

Purification was effected through the ethyl ester, which was prepared as described below, purified by distillation, and rehydrolysed by boiling with hydrochloric acid until no more alcohol was evolved and then evaporating on a water-bath. The yield of pure acid was 50 per cent. of the theoretical.

The Monohydrate.—The pure acid crystallises from very concentrated aqueous solution in needles, melting with decomposition at 181°, and containing one molecule of water of crystallisation (Found: $C = 38·3$; $H = 4·75$. $C_8H_{10}O_8,H_2O$ requires $C = 38·1$; $H = 4·75$ per cent.). On keeping in a dry atmosphere, part of the water of crystallisation is rapidly lost.
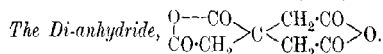
The Anhydrous Acid.—The hydrate was heated for two hours at 120° and the residue recrystallised from a mixture of acetone and chloroform, from which the anhydrous acid separated in minute crystals melting with decomposition at 208—210° (Found: $C = 40·7$; $H = 4·5$. $C_8H_{10}O_8$ requires $C = 41·0$; $H = 4·3$ per cent.).

The Barium Salts.—The acid forms a very characteristic barium salt, which, although it separates with water of crystallisation, is exceedingly insoluble in hot or cold water and can be precipitated by adding aqueous barium hydroxide to a solution of the ammonium salt even at considerable dilutions. The precipitate, after drying at 95°, consists of the *trihydrate* (Found: $Ba = 48·9$. $C_8H_6O_8Ba_2,3H_2O$ requires $Ba = 49·1$ per cent.), but if it be dried

to constant weight at 160°, the *monohydrate* will be obtained (Found: Ba = 52·45. $C_8H_6O_8Ba_2,H_2O$ requires Ba = 52·5 per cent.). The *anhydrous* salt is formed when either of the hydrates is heated to constant weight at 220° (Found: Ba = 54·1. $C_8H_6O_8Ba_2$ requires Ba = 54·3 per cent.).

Ethyl Carboxymethanetriacetate.

Carboxymethanetriacetic acid is not readily converted into its tetraethyl ester by the ordinary methods of esterification, and the following process was therefore resorted to. The crude acid (165 grams) was mixed with 400 c.c. of ethyl alcohol and 50 c.c. of concentrated sulphuric acid in a flask fitted with a 10 cm.-fractionating column and a condenser. A stream of ethyl alcohol vapour was passed into the flask, which was kept in an oil-bath at 120° until 4 litres of distillate had collected. The reaction mixture was then cooled and poured into ice-cold water, and the esters were extracted by means of ether, separated from acid products by sodium carbonate solution in the usual manner, and purified by distillation under diminished pressure. In this way 156 grams of the pure ester, b. p. 208°/15 mm. (Found: C = 55·3; H = 7·5. $C_{16}H_{26}O_8$ requires C = 55·5; H = 7·5 per cent.), were obtained together with a small amount of "low fraction," consisting largely of the same substance, and 10 grams of a mixture of acid esters which yielded the same carboxymethanetriacetic acid on hydrolysis.

$$\text{The } \textit{Di-anhydride,} \quad \begin{matrix} O---CO \\ | \\ CO \cdot CH_2 \end{matrix} > C < \begin{matrix} CH_2 \cdot CO \\ CH_2 \cdot CO \end{matrix} > O.$$

This substance was prepared by boiling the acid (or its monohydrate) with an excess of acetic anhydride for one hour, and distilling off the acetic acid under diminished pressure at 100°. The residue solidified on keeping, and the solid, after recrystallisation from acetone, melted at 223° with slight decomposition. It was insoluble in water, but dissolved slowly in sodium carbonate solution, forming sodium carboxymethanetriacetate (Found: C = 48·1; H = 3·2. $C_8H_6O_6$ requires C = 48·5; H = 3·0 per cent.).

It will be observed that this anhydride melts at a higher temperature than the corresponding acid, a circumstance which is very unusual, but not unknown; two other instances of the same phenomenon are afforded by ββ-dimethylglutaric and camphoric anhydrides.

(B) Oxidation of cycloPentane-1 : 1-diacetic Acid.

Very little need be said regarding our experiments on the oxidation of *cyclo*pentane-1 : 1-diacetic acid, since the method of working

was the same as that already described in connexion with the oxidation of its ring-homologue and the sole product was the carboxymethanetriacetic acid already dealt with. It should be noted, however, that the acid $C_9H_{12}O_8$ appeared not to be produced under any of the conditions used, and also, for it is of theoretical interest in connexion with a modification of the "Spannungs. theorie" recently suggested (Ingold, this vol., p. 305), that so far as we could judge there is no considerable difference in the case of fission by oxidation of the homocyclic rings present in *cyclo*pentane. and *cyclo*hexane-1 : 1-diacetic acids.

We are greatly indebted to Professor J. F. Thorpe for the interest which he has taken in this work and also for much valuable advice. We wish to thank the Chemical Society for a grant which has defrayed a large part of the cost of the investigation.

CCXIV.—*Dichloroacetates and Chlorobromoacetates from αβ-Dichlorovinyl Ethyl Ether.*

By HOLLAND CROMPTON and PHYLLIS MARY TRIFFITT.

CHLORINE is readily absorbed by αβ-dichlorovinyl ethyl ether at the ordinary temperature. If care is taken to exclude moisture, the product, on heating, or on keeping for some time, breaks up into dichloroacetyl chloride and ethyl chloride,

$$CHCl{:}CCl{\cdot}OEt + Cl_2 = CHCl_2{\cdot}COCl + EtCl.$$
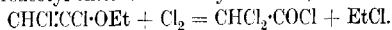
If water is added, or if the product is left exposed to the air, when moisture will be absorbed, on heating or on keeping hydrogen chloride is evolved, and on distillation ethyl dichloroacetate is obtained in almost theoretical yield,

$$CHCl{:}CCl{\cdot}OEt + Cl_2 + H_2O = CHCl_2{\cdot}CO_2Et + 2HCl.$$
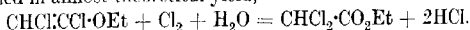
The action of bromine on αβ-dichlorovinyl ethyl ether is similar to that of chlorine. With perfectly dry materials and careful exclusion of water, chlorobromoacetyl chloride, b. p. 138—139°, and ethyl bromide are obtained. If free access of moisture is allowed, ethyl chlorobromoacetate, b. p. 174°, d_4^{x} 1·5890, is produced, along with hydrogen chloride and hydrogen bromide.   •

From the behaviour of chlorinated and brominated dichlorovinyl ethyl ether with water, it seemed likely that the substitution of alcohols or phenols for water in the above reactions would lead

to the production of esters of dichloroacetic and chlorobromoacetic acids. This was found to hold for ethyl and amyl alcohols and for a number of phenols. Aryl dichloroacetates and chlorobromo-acetates are usually solids at the ordinary temperature, crystallising readily from the reaction product and obtainable in good yield.

Corresponding aryl dichloroacetates and chlorobromoacetates appear to be isomorphous and to form mixed crystals with one another in all proportions. The melting points of these compounds are also almost identical, the replacement of a chlorine atom in the dichloroacetate by a bromine atom having only a slight effect on the melting point. This is shown in the case of the phenyl derivatives.

Phenyl dichloroacetate, m. p. 48°, b. p. 247·5° (corr.), d_4^{20} 1·2991.
Phenyl chlorobromoacetate, m. p. 46·5°, b. p. 266° (corr.), d_4^{20} 1·5311.

The melting points are those determined in the ordinary way. The solidifying or freezing points of these compounds, and of their mixtures with one another in varying proportions, are given in the following table :

Molecular percentage of		Freezing Points.	
Dichloroacetate.	Chlorobromoacetate.	Obs.	Cal.
100	0	46·25°	···
91·7	8·3	45·9	46·0
83·1	16·9	45·5	45·8
75·3	24·7	45·0	45·6
56·3	43·7	44·7	45·1
31·9	68·1	44·2	44·5
20·0	80·0	44·05	44·2
9·8	90·2	43·9	44·0
0	100	43·7	···

The numbers given in the last column are those calculated on the assumption that the freezing points of the mixtures, when plotted against molecular percentages, lie on a straight line connecting the freezing points of the two components. As is usual in cases of this kind, the observed values are slightly lower than the calculated.

In the other cases examined it was not found possible to detect a difference between the melting points of corresponding aryl compounds determined in the usual way. These cases were :

p-Tolyl dichloroacetate and chlorobromoacetate, m. p. 58°.

β-Naphthyl dichloroacetate and chlorobromoacetate, m. p. 92—93°.

Quinol bisdichloroacetate and bischlorobromoacetate, m. p. 123—124°.

The corresponding compounds can be mixed with one another in any proportion with no appreciable effect on the melting point.

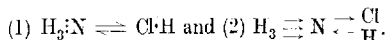BEDFORD COLLEGE,
REGENT'S PARK, N.W.1.

CCXV.—*Valency and Co-ordination.*

By SAMUEL HENRY CLIFFORD BRIGGS.

As an attempt has recently been made to show that Werner's conception of co-ordination is of a more fundamental character than hitherto supposed (Briggs, *Phil. Mag.*, 1921, **42**, 448), it seems desirable to refer to some criticisms of Werner's views brought forward by Rhodes (*Chem. News*, 1921, **122**, 85, 97) and by Friend (this vol., p. 1042).

(1) Rhodes objects to Werner's formula for ammonium chloride, chiefly on the ground that the position of the chlorine in $(NH_4)Cl$ suggests instability, the chlorine being combined with the complex as a whole rather than with an individual atom in the complex. When it is remembered, however, that the ammonium radicle and the chloride ion possess equal and opposite electrical charges, the stability of the compound is not difficult to understand.

Friend suggests that ammonium chloride exists in two forms

$$(1)\ H_3\dot{:}N \rightleftharpoons Cl\cdot H \text{ and } (2)\ H_3 \rightleftharpoons N \overset{\longrightarrow}{\underset{\cdot\cdot}{}} \overset{Cl}{\underset{H}{}}.$$

According to Werner (" Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," 3rd. ed., p. 248) ". . . die Entstehung von Chlorammonium folgendermassen wiederzugeben ist

$$\begin{array}{c} H \\ H \\ H \end{array}\!\!\!\!>\!N + HCl = \begin{array}{c} H \\ H \\ H \end{array}\!\!\!\!>\!N\cdots HCl$$
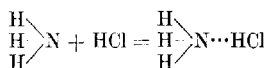
. . . und da es unwahrscheinlich ist dass ein Wasserstoffatom durch einen anderen Affinitätsbetrag an Stickstoff gekettet ist als die drei anderen, so wird sich im Affinitätsausgleich ein Endzustand herausbilden, bei dem sämtliche Wasserstoffatome durch gleiche Affinitätsbeträge an dem Stickstoff gebunden sind. Das Ammonium ist hiernach ein komplexes Radical, NH_4, in dem ein zentrales Stickstoffatom vier Wasserstoffatome jedes mit gleichem Affinitätsbetrag, bindet . . . . Strukturchemisch ist das Chlorammonium deshalb durch folgendes Symbol wiederzugeben

$$\begin{bmatrix} H\cdot\ \cdot H \\ N \\ H\cdot\ \cdot H \end{bmatrix} Cl"\ (2)$$
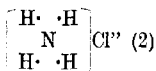
The existence of ammonium chloride in two forms is therefore

quite possible on Werner's theory, but Werner's formula (2) appears preferable to Friend's second formula, because the chlorine atom is ionisable, whereas the hydrogen atoms are not.

(2) In the writer's opinion, Werner's formula for the carbonato-pentamminecobaltic salts is not a violation of the co-ordination theory, as suggested by Friend. One of the negatively-charged oxygen atoms of the carbonate ion is linked to the cobalt and the other charged atom is not linked up and will therefore be analogous to a charged atom (anion) outside the complex, as shown in Werner's formula. The carbonato-radicle, however, will not give free carbonate ions in solution owing to the non-ionisable union of *one* oxygen atom with the central cobalt atom.

(3) The shell theory suggested by Friend for complex compounds is open to criticism on the following grounds.

(*a*) If the ammonia molecules in $Co(6NH_3)Cl_2$ and $(Co6NH_3)Cl_3$ are not attached to the cobalt atom, but are linked up to each other to make a shell, there is no apparent reason for the great difference in stability of the compounds. But if they are attached to the cobalt as required by Werner's theory, it follows from the electrical theory of the atom that the cobaltic compound is more stable than the cobaltous salt, as is actually the case (Briggs, T., 1917, **111**, 253).

(*b*) On Friend's shell theory, there is no explanation of Werner's maximum co-ordination numbers 4, 6, 8 (and 12). The writer has shown, however, that if the co-ordinated atoms or groups are directly attached to the central atom as required by Werner, then the maximum co-ordination numbers follow on geometrical grounds from Rutherford's theory of the atom with a positive nucleus (T., 1919, **115**, 278).

(*c*) Friend's shell theory, when applied to the salts of complex acids, requires isomerism due to differences in the points of attachment of the positive atoms. The writer held the view that such isomerism might be possible in a paper on duplex affinity published some years ago, formula I being given to potassium platinichloride (T., 1908, **93**, 1564). In later papers, the theory was developed further on the assumption that positive affinity is a tendency to lose electrons, and negative affinity a tendency to attract electrons. With such an assumption we can only expect that in the complex ion $PtCl_6''$ the chlorine atoms will all become electrically equal, and that consequently the potassium atoms will be united to the complex as a whole, as seen in formula II and as required by Werner's theory, instead of to distinct chlorine atoms, as shown in formula I and as is also required by Friend's theory. Stereoisomerism should not therefore be possible.

$$\cdots\rightarrow \text{KCl} \rightarrow \quad \underset{\text{(I.)}}{\text{Pt}} \begin{array}{l} = \text{Cl} \\ = \text{Cl} \\ \rightleftharpoons \text{Cl} \\ \rightleftharpoons \text{Cl} \\ = \text{Cl} \end{array} \qquad \cdots\rightarrow \underset{\text{(II.)}}{\text{K}_2^{\cdot}(\text{Pt}^{\cdots\cdot} \leftarrow \text{Cl}_6' \longrightarrow)}$$

The question can, however, be decided only by experimental investigation, and the writer has been engaged for some years in the study of such supposed cases of isomerism. It has been already shown that Marignac's second form of potassium stannifluoride is potassium hydroxopentafluorostanneate, $K_2(SnF_5OH)$ (*Zeitsch. anorg. Chem.*, 1913, **82**, 441), that Locke and Edwards's second form of potassium ferricyanide is a compound of the formula $3K_3Fe(CN)_6,K_2[Fe(CN)_5H_2O]$, and that the second form of potassium ferrocyanide observed by the writer is the ordinary ferrocyanide containing a trace of aquopentacyanoferroate (T., 1920, **117**, 1026). The remaining cases of the two aquopentachlororutheniates and the two hexachlororutheneates are now being investigated. It has been found that the formula for the first pair of isomerides is not K_2RuCl_5,H_2O, but $2K_2RuCl_5,3H_2O$, and it will be shown in a subsequent paper that these can be brought into agreement with Werner's theory. The existence of two salts of the formula K_2RuCl_6 appears doubtful, but the investigation is not yet completed.

(*d*) The difficulty of Friend's shell theory, and indeed of all other valency theories in dealing with strong electrolytes, is apparent if we consider a crystal of sodium chloride in which every sodium ion is surrounded by six chloride ions, and every chloride ion by six sodium ions. It is difficult to imagine a system of two interpenetrating shell lattices, one made up of positively charged sodium atoms linked to each other, and the other of negatively charged chlorine atoms united together. On the other hand, if we write a valency formula with each sodium ion united to six chloride ions, and each chloride ion linked to six sodium ions, as is actually the case, then we must either assume that chlorine and sodium are both sexavalent, or that they each possess six partial valencies, the six being equal to one whole valency. Werner's co-ordination theory is much more satisfactory than any valency theory in this respect, and can be applied to such crystal structures (Pfeiffer, *Zeitsch. anorg. Chem.*, 1915, **92**, 376; 1916, **97**, 161).

(4) Friend's free valency and residual valency and Thomson's ionised valency and non-ionised valency really represent two extreme types of combination, as is emphasised by Friend (*loc. cit.*, p. 1043) (compare Briggs, T., 1917, **111**, 267). The same argument applies equally to Langmuir's clean-cut division of valency into

electrovalence, in which the charged atoms are held together by electrostatic force, and *co-valence*, in which the atoms are united owing to the sharing of electrons. Since the electrons are united to the kernel of an atom by electrostatic force, it would appear that electrostatic attraction between two charged atoms, that is, electrovalence, involves the sharing of electrons, and the distinction between electrovalence and co-valence is therefore one of degree rather than of kind. Co-valence represents a condition in which electrons are shared equally between two atoms, and electrovalence a condition of unequal sharing, the more unequal the sharing of the electrons the greater the tendency of the compound to undergo electrolytic dissociation.

<div align="right">[*Received, October 12th*, 1921.]</div>

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CCXVI.—*Studies in the* n-*Butyl Series.   Part I.* *Aryl* n-*Propyl Ketones.*

By GILBERT T. MORGAN and WILFRED JOHN HICKINBOTTOM.

THE industrial development during recent years of a fermentation yielding *n*-butyl alcohol has rendered available considerable amounts of this alcohol, for which sufficient use has not hitherto been found. A consideration of the problem of the utilisation of this product leads to the conclusion that the solution lies in the employment of derivatives of *n*-butyl alcohol rather than in its use as a substitute for fusel oil. It is from this point of view that we have examined the properties of certain *n*-butyl compounds derived by practicable processes from *n*-butyl alcohol.

The influence of butyl and butyryl groups in enhancing the odour of chemical substances is well known, and aryl derivatives containing these osmophoric radicles have been prepared and examined. On comparing the odours of the substituted *n*-butylbenzene with those of the corresponding derivatives of phenyl *n*-propyl ketones, it is noticed that the odour diminishes in intensity on passing from the hydrocarbon to the ketone. This is particularly noticeable with the nitro-derivatives. 3-*Nitrophenyl* n-*propyl ketone,* for instance, is almost inodorous, whilst the nitro-*n*-butylbenzenes and 2-*nitro*-1 : 4-*di*-n-*butylbenzene* have characteristic odours. Orientation has its effect, for 2-*nitrophenyl* n-*propyl ketone* has a pleasant odour, which is, however, less fragant than that of the corresponding nitro-derivative of *n*-butylbenzene.
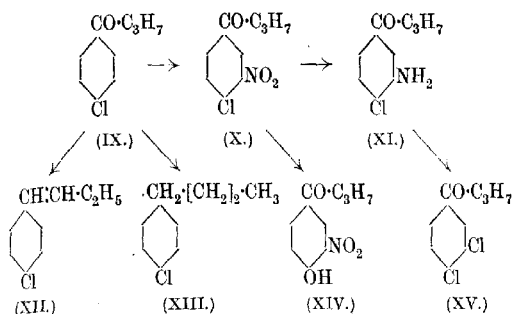
This contrast is not in accordance with the osmophoric theory of Rupe and Majewski (*Ber.*, 1900, **33**, 3401; compare also Klimont, " Die Synthetische und Isolierten Aromatica "), for it might be expected that the presence of two osmophores, $-CO\cdot CH_2-$ and $-NO_2$, would give rise to a substance having an odour at least as intense as that of the nitrohydrocarbon. This anomaly is explicable on the assumption that in the aromatic series the effect of an osmophoric grouping is variable, depending, among other factors, on the presence of other osmophores in the molecule and also on their relative positions, so that the odour of a compound containing more than one osmophoric group in its molecule may be either increased or diminished as the orientation of the substituent varies. This influence of orientation is illustrated by a comparison of the odours of various derivatives of phenyl *n*-propyl ketone. Substitution in the *meta*-position yields, as a rule, substances with faint odours, whilst the corresponding *ortho*-compounds generally possess powerful and characteristic odours. It is noteworthy that 2-aminophenyl *n*-propyl ketone, which is an odoriferous substance, contains the grouping characteristic of methyl anthranilate,

, where $R = C_3H_7$ or $\cdot O\cdot CH_3$ (compare Rupe and Majewski, *Ber.*, 1900, **33**, 3401).
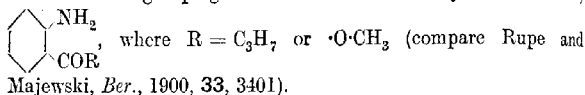
Butyryl chloride was condensed in turn with benzene, chlorobenzene, and *m*-xylene; the resulting ketones were converted successively into their nitro- and amino-derivatives. In the case of phenyl *n*-propyl ketone (II) nitration follows the *meta*-law of substitution, the *meta*-nitro-compound (III) is the main product, but the formation of a small proportion of the *ortho*-nitro-derivative (I) was noticed.
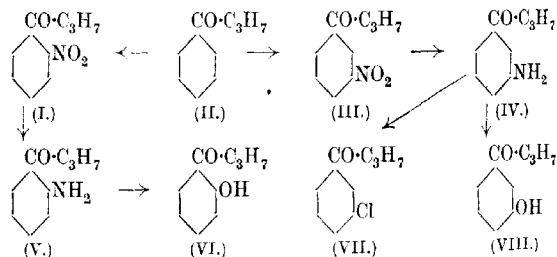
With p-*chlorophenyl* n-*propyl ketone* (IX) the nitro-group enters exclusively the *ortho*-position with respect to chlorine, yielding 4-*chloro*-3-*nitrophenyl* n-*propyl ketone* (X).

$CO \cdot C_3H_7$ $CO \cdot C_3H_7$ $CO \cdot C_3H_7$

Cl $\rightarrow$ NO$_2$ $\rightarrow$ NH$_2$

Cl   Cl   Cl

/ (IX.) \   (X.) \   (XI.) \
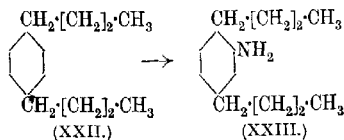
CH:CH·C$_2$H$_5$ ·CH$_2$·[CH$_2$]$_2$·CH$_3$ $CO \cdot C_3H_7$ $CO \cdot C_3H_7$

Cl   Cl   NO$_2$ Cl

Cl   Cl   OH   Cl

(XII.)   (XIII.)   (XIV.)   (XV.)

In the case of m-4-xylyl n-propyl ketone (butyro-2 : 4-dimethyl-phenone, XVI), nitration occurs as with the parent aromatic hydrocarbon, m-xylene; the main product is 6-*nitro*-m-4-*xylyl* n-*propyl ketone* (XVII), whereas 2-*nitro*-m-4-*xylyl* n-*propyl ketone* (XIX) is formed in smaller proportion. Further nitration leads to 2 : 6-*dinitro*-m-4-*xylyl* n-*propyl ketone* (XX).

$CO \cdot C_3H_7$ $CO \cdot C_3H_7$ $CO \cdot C_3H_7$

CH$_3$ $\rightarrow$ NO$_2$ CH$_3$ $\rightarrow$ NH$_2$ CH$_3$

CH$_3$ CH$_3$ CH$_3$

| (XVI.) | (XVII.) | (XVIII.)

$CO \cdot C_3H_7$ $CO \cdot C_3H_7$ $CO \cdot C_3H_7$

CH$_3$ $\rightarrow$ NO$_2$ CH$_3$ Cl CH$_3$
NO$_2$ NO$_2$

CH$_3$ CH$_3$ CH$_3$

(XIX.)   (XX.)   (XXI.)
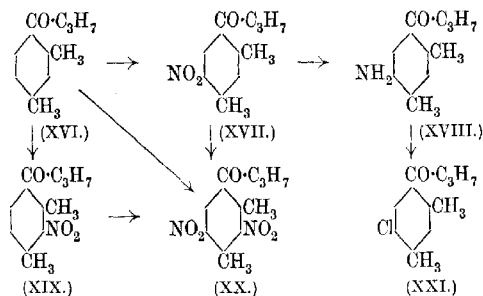
In the foregoing condensations to form mixed ketones the introduction of the butyryl group into the benzene ring through the agency of the Friedel and Crafts reaction occurs much more smoothly than the substitution of a butyl group for chlorine by the Fittig reaction in the formation of p-*di*-n-*butylbenzene* (XXII) from p-dichlorobenzene.

CH$_2$·[CH$_2$]$_2$·CH$_3$ CH$_2$·[CH$_2$]$_2$·CH$_3$

NH$_2$ $\rightarrow$

CH$_2$·[CH$_2$]$_2$·CH$_3$ CH$_2$·[CH$_2$]$_2$·CH$_3$

(XXII.)   (XXIII.)

Accordingly, the mixed ketones have been submitted to a more detailed examination.

EXPERIMENTAL.

I. *Phenyl* n-*Propyl Ketone.*

Phenyl n-propyl ketone was prepared in a 69 per cent. yield by the interaction of n-butyryl chloride * and an excess of benzene in presence of aluminium chloride. Phenyl n-propyl ketone was characterised by its p-*nitrophenylhydrazone*, which separated from glacial acetic acid in orange-red, prismatic needles having a metallic blue reflex; it melted at 163° (Found : N = 15·13. $C_{16}H_{17}O_2N_3$ requires N = 14·84 per cent.).

1. *Nitration in Acetic Anhydride.* 3-*Nitrophenyl* n-*Propyl Ketone* (III).—Phenyl n-propyl ketone (5·2 grams) was cautiously added with continuous stirring to 33 grams of fuming nitric acid mixed with 32 grams of acetic anhydride, the temperature being maintained below 5°. After half an hour, the nitration mixture was poured on to crushed ice, when crude 3-nitrophenyl n-propyl ketone was precipitated as a white, curdy solid, which was pressed from oily by-products. The nitrated ketone separated from warm alcohol in white, brittle plates melting at 61° (Found : C = 61·73; N = 7·53. $C_{10}H_{11}O_3N$ requires C = 62·15; N = 7·25 per cent.). It was not readily soluble in light petroleum or cold alcohol, but more readily so in ether or chloroform. 3-Nitrophenyl n-propyl ketone was oxidised to m-nitrobenzoic acid on heating with chromic acid or potassium permanganate in presence of dilute sulphuric acid; it yielded a *phenylhydrazone* crystallising from alcohol in orange-red masses of small needles melting at 103°. The p-*nitrophenylhydrazone* was deposited from warm glacial acetic acid in minute, pale yellow crystals melting at 205° (Found : N = 17·28. $C_{16}H_{16}O_4N_4$ requires N = 17·07 per cent.).

2-*Nitrophenyl* n-*Propyl Ketone* (I).

The oily filtrates and washings from the 3-nitro-compound were repeatedly extracted with ether to remove the liquid product of the nitration. The ethereal extract was washed with aqueous sodium hydroxide solution and the solvent evaporated. The residual oil contained a mixture of the 2- and 3-nitro-compounds, from which the greater part of the solid isomeride was removed by freezing. There was not sufficient material available to attempt

* Our thanks are due to Captain Desborough, of the Royal Naval Cordite Factory, for the n-butyl alcohol required in this investigation.

the lengthy fractionation under diminished pressure which appeared necessary to isolate the *ortho*-nitro-compound in a pure state, and recourse was made to the difference in behaviour of the isomerides with *p*-nitrophenylhydrazine. Crude 2-nitrophenyl *n*-propyl ketone was heated in a boiling water-bath with three-fifths of its weight of *p*-nitrophenylhydrazine in alcoholic solution. A dark red oil resulted which slowly deposited the *p*-nitrophenylhydrazone of the 3-nitro-compound as a reddish-yellow solid. The separation was hastened by treatment with dry ether, when, on submitting the residue to distillation in a current of steam, a pale yellow oil passed over, which was subjected to further treatment with *p*-nitrophenyl-hydrazine. It was finally purified by two steam distillations in presence of dilute hydrochloric acid. By these means 2-*nitrophenyl n-propyl ketone* was obtained as a pale yellow oil having a sweet odour resembling to some extent that of nitrobenzene (Found : $N = 7.01$. $C_{10}H_{11}O_3N$ requires $N = 7.25$ per cent.).

In the nitration of phenyl *n*-propyl ketone with nitric acid and acetic anhydride, the yield of mixed nitro-compounds after removing *iso*nitroso-compounds and oxidation products amounted to 97—98 per cent. of the calculated amount.

2. *Nitration in Sulphuric Acid.*—A mixture of 1·1 to 1·2 molecular proportions of nitric acid (d 1·42) and concentrated sulphuric acid (18 grams) was added with continuous stirring to phenyl *n*-propyl ketone (5·4 grams) dissolved in 60 grams of concentrated sulphuric acid, the temperature being maintained below 5° throughout the operation. The mixture was left at 0° for about two hours and then poured on to ice. The isolation of 3-nitrophenyl *n*-propyl ketone was effected as in the preceding preparation.

3-*Aminophenyl* n-*propyl ketone* (IV), obtained in good yield by the reduction of the corresponding nitro-compound with zinc dust and ammonium chloride in aqueous alcoholic solution, was purified by fractionation under diminished pressure; it distilled over as a pale yellow, viscous oil at 194—197°/29—30 mm. and solidified to a white mass of crystals melting at 27—28° (Found : $N = 8.30$. $C_{10}H_{13}ON$ requires $N = 8.59$ per cent.).

The *hydrochloride* separated from its concentrated solution in hydrochloric acid in masses of colourless needles, but was hydrolysed in aqueous solution. The *zincichloride* was precipitated as a white, sparingly soluble mass by the addition of an aqueous solution of zinc chloride to a suspension of the base. The *picrate* separated from warm benzene in bright yellow nodules or rosettes of needles melting at 132—133° (Found : $N = 14.44$. $C_{10}H_{13}ON,C_6H_3O_7N_3$ requires $N = 14.28$ per cent.).

3-*Acetylaminophenyl* n-*propyl ketone*, prepared by warming the

base with acetic anhydride, separated from a mixture of benzene and light petroleum in plates melting at 71·5—72·5° (Found: N = 7·02. $C_{12}H_{15}O_2N$ requires N = 6·83 per cent.).

3-*Benzoylaminophenyl* n-*propyl ketone* separated from warm aqueous alcohol in small, white crystals melting at 103—104° (Found : N = 5·17. $C_{17}H_{17}O_2N$ requires N = 5·24 per cent.).

n-*Butyrophenone*-3-*azo*-β-*naphthol*, obtained by coupling 3-diazo-phenyl n-propyl ketone chloride with β-naphthol in alkaline solution, crystallised from warm alcohol in small, red needles having a faint green reflex (m. p. 127—128°) (Found : N = 9·05. $C_{20}H_{18}O_2N_2$ requires N = 8·80 per cent.). It gave a crimson coloration in concentrated sulphuric acid.

n-*Butyrophenone*-3-*azo*-β-*naphthylamine*, produced as in the preceding preparation, using an alcoholic solution of β-naphthylamine, crystallised from warm glacial acetic acid in orange-red plates or scales having a coppery lustre, or on slow cooling in small, acicular plates arranged in clusters. It melted at 149—150° (Found: N = 13·51. $C_{20}H_{19}ON_3$ requires N = 13·25 per cent.). This *azo*-β-*naphthylamine* developed in concentrated sulphuric acid a violet-blue coloration, changing to red and brown on dilution. Concentrated hydrochloric acid in glacial acetic acid gave rise to a bright red coloration.

n-*Butyrophenone*-3-*azoresorcinol*.—The diazotised amino-ketone was coupled with resorcinol in either aqueous or alcoholic solution in presence of sodium acetate, when the crude *azo*-compound separated. It was purified by precipitation from its solution in dilute sodium hydroxide and finally by crystallisation from warm benzene, when it separated as an orange-red powder melting at 144° (Found : N = 10·10. $C_{16}H_{16}O_3N_2$ requires N = 9·86 per cent.). A small amount of another *azo*-compound was obtained, which was insoluble in aqueous alkalis, but soluble in alcoholic potassium hydroxide. It separated from alcohol as a bright red, sparingly soluble powder. Sulphuric acid developed a red coloration.

3-*Hydroxyphenyl* n-*Propyl Ketone* (VIII).—On boiling the diazo-tised solution from 3-aminophenyl n-propyl ketone with an excess of diluted sulphuric acid, 3-*hydroxyphenyl* n-*propyl ketone* separated as a dark oil, becoming solid on cooling; it was purified by solution in dilute sodium hydroxide and precipitation with acid, followed by crystallisation from warm light petroleum. It crystallised from a mixture of benzene and light petroleum in white, rhombic plates melting at 63° (Found : C = 73·10; H = 7·46. $C_{10}H_{12}O_2$ requires C = 73·13; H = 7·38 per cent.). 3-Hydroxyphenyl n-propyl ketone, which has only a faint, pleasant, phenolic odour, coupled with diazotised p-nitroaniline to yield a red *azo*-compound.

The p-*nitrophenylhydrazone* of 3-hydroxyphenyl *n*-propyl ketone crystallised from benzene in orange-yellow needles melting at 160° (Found : N = 14·17. $C_{16}H_{17}O_3N_3$ requires N = 14·04 per cent.).

3-*Chlorophenyl* n-*propyl ketone* (VII), an almost colourless oil volatile in steam, was obtained from the corresponding amino-compound by the Sandmeyer reaction. Its odour resembled that of 4-chlorophenyl *n*-propyl ketone (IX), but was less intense (Found : Cl = 19·15. $C_{10}H_{11}OCl$ requires Cl = 19·42 per cent.).

The p-*nitrophenylhydrazone* separated from glacial acetic acid in minute, dull yellow crystals melting at 138° (Found : N = 13·58. $C_{16}H_{16}O_2N_3Cl$ requires N = 13·23 per cent.).

2-*Aminophenyl* n-*Propyl Ketone* (V).—By reducing 2-nitrophenyl *n*-propyl ketone (I) with zinc dust and ammonium chloride in boiling alcoholic solution, this amine was obtained as a pale yellow oil, volatile in steam and possessing a characteristic and pleasant odour when dilute. On adding concentrated hydrochloric acid to the base, the *hydrochloride* separated in clusters of white, prismatic needles melting at 160—162° to a dark red liquid. It darkened a few degrees below its melting point (Found : N = 6·95; Cl = 17·75. $C_{10}H_{13}ON,HCl$ requires N = 7·01; Cl = 17·76 per cent.). The amine was readily obtained by the reduction of the liquid product of the nitration of phenyl *n*-propyl ketone. On distilling the mixture of amines in a current of steam, the *ortho*-compound passed over the more readily, and was obtained pure by crystallising its hydrochloride two or three times from concentrated hydrochloric acid.

The amine was diazotised readily in dilute hydrochloric acid solution, and on pouring the solution of the diazonium salt into alkaline β-naphthol the *azo*-β-*naphthol* separated as a bright red powder, which crystallised from warm alcohol in bright red masses of small crystals having a faint metallic reflex. It melted at 154—155° (Found : N = 9·10. $C_{20}H_{18}O_2N_2$ requires N = 8·80 per cent.). The *azo*-compound developed a violet coloration in concentrated sulphuric acid.

On boiling a solution of the diazotised amine with excess of dilute sulphuric acid, 2-*hydroxyphenyl* n-*propyl ketone* (VI) separated as a pale yellow, viscous liquid, which was purified by solution in alkali followed by distillation in a current of steam (Found : C = 73·24; H = 7·13. $C_{10}H_{12}O_2$ requires C = 73·13; H = 7·39 per cent.).

II. 4-*Chlorophenyl* n-*Propyl Ketone* (IX).

n-Butyryl chloride (30 grams) was added gradually with continuous stirring to 83 grams of chlorobenzene mixed with freshly-prepared aluminium chloride (35 grams), the temperature being

maintained at 40—60°. After four hours, the product was poured on to ice and the pale yellow oil, having been washed with aqueous sodium hydroxide solution, was distilled, when it gave a colourless fraction at 253—254° (uncorr.) which solidified on cooling to a mass of crystalline and practically pure *4-chlorophenyl* n-*propyl ketone* (yield 72 per cent.); this product separated from alcoholic solution in white, soft, tabular crystals melting at 36° (Found : Cl = 19·29. $C_{10}H_{11}OCl$ requires Cl = 19·42 per cent.). The ketone, which was soluble in the common organic media, was characterised by a pleasant odour more powerful than that of phenyl n-propyl ketone.

Oxidation of 4-chlorophenyl n-propyl ketone with sodium di-chromate and dilute sulphuric acid gave p-chlorobenzoic acid, thereby establishing the orientation of the chlorine substituent with respect to the ketonic group.

The *phenylhydrazone* crystallised from alcohol in white, slender needles melting at 85° (Found : N = 9·20. $C_{16}H_{17}N_2Cl$ requires N = 10·27 per cent.). This hydrazone was found to be unstable, a pure specimen becoming converted into a dark brown tar after one month in a closed tube.

The p-*nitrophenylhydrazone* separated from a mixture of benzene and alcohol in small, yellow crystals melting at 173—174° (Found : N = 13·39. $C_{16}H_{16}O_2N_3Cl$ requires N = 13·23 per cent.).

Reduction of 4-Chlorophenyl n-Propyl Ketone.

(a) *4-Chloro-*n-*butylbenzene.*—The reduction was carried out at 80—100° with hydrochloric acid and amalgamated zinc, according to Clemmensen's method for the reduction of ketones to hydro-carbons (*Ber.*, 1913, **46**, 1838). After twelve hours, the insoluble, yellow oil was removed and distilled in a current of steam. In the distillate crude 4-chloro-n-butylbenzene (XIII) was obtained, which was fractionally distilled after being separated and dried. The main distillate was collected at 225—228°/761 mm. as a colour-less, refractive liquid stable to cold neutral permanganate solution and possessing a powerful odour of anise (Found : Cl = 20·72. $C_{10}H_{13}Cl$ requires Cl = 21·03 per cent.).

4-Chlorobutenylbenzene (XII).—In the reduction of the ketone by Clemmensen's method a small quantity of an unsaturated compound was usually obtained, the yield of which was increased by continuing the reduction for a shorter period or by working at a lower temperature. Under these conditions a mixture of 4-chlorobutenylbenzene and 4-chloro-n-butylbenzene was obtained in the fraction distilling between 225° and 240°. As the difference in the boiling points of the two substances was inconsiderable, and

as the quantity of available material did not permit of a systematic fractionation, evidence of the presence in the mixture of 4-chlorobutenylbenzene was obtained by converting the compound into its dibromide. That portion of the crude reaction product which was volatile in steam was suspended in water and treated with bromine until there was no further absorption. The heavy oil which resulted, having been treated with sodium sulphite solution, was distilled in steam, when a pasty, non-volatile residue (*b*) was obtained on cooling. The liquid portion volatile in steam was separated by distillation into 4-chloro-*n*-butylbenzene (*a*) and a liquid (*c*) boiling with decomposition above 230° and having a fragrant odour of hyacinths. Since the liquid (*c*) contained bromine and yielded *4-chlorobutenylbenzene* on boiling with anhydrous pyridine for seven hours, it was probably *4-chlorobromobutylbenzene*.

4-Chlorobutenylbenzene, a colourless, refractive liquid boiling at 234—237°/749 mm., had an odour resembling that of the saturated hydrocarbon (*a*), except that it was less pronounced and somewhat alliaceous (Found: $Cl = 21.16$. $C_{10}H_{11}Cl$ requires $Cl = 21.28$ per cent.).

(*b*) 4-*Chloro-αβ-dibromo-*n-*butylbenzene.*—The pasty residue (*b*) obtained in the foregoing steam distillation was drained and crystallised from alcohol, when the purified dibromide separated in transparent prisms melting at 72° (Found: $AgCl + AgBr = 159.6$. $C_{10}H_{11}ClBr_2$ requires $AgCl + AgBr = 159.0$ per cent.).

The reduction of 4-chlorophenyl *n*-propyl ketone with amalgamated zinc and hydrochloric acid gave a varying proportion of a vitreous residue, not volatile in steam. By substituting for aqueous hydrochloric acid a solution of one part of concentrated hydrochloric acid in two parts of alcohol, the amount of by-product was increased. The substance was only sparingly soluble in alcohol, but more readily so in benzene or light petroleum. It melted indefinitely at 55—60° and was presumably a *polymeride* of 4-chlorobutenylbenzene.

4-*Chloro-*3-*nitrophenyl* n-*Propyl Ketone* (X).—It was found necessary to carry out the nitration of 4-chlorophenyl *n*-propyl ketone at a temperature not exceeding −5°, in order to reduce the tendency to oxidation.

4-Chlorophenyl *n*-propyl ketone (2 grams) dissolved in 18 grams of sulphuric acid (*d* 1·84) was cautiously added to a mixture of 15 grams of nitric acid (*d* 1·42) and 36 grams of concentrated sulphuric acid, cooled to −12° and constantly stirred. After the ketone had been added, the nitration mixture was left for a period of ten to thirty minutes and then poured on to crushed ice. The white, curdy solid, after being washed with water and sodium

carbonate solution, was purified by crystallisation from alcohol, when it separated in white plates melting at 53° (Found : $N = 6.34$; $Cl = 15.25$. $C_{10}H_{10}O_3NCl$ requires $N = 6.15$; $Cl = 15.58$ per cent.).

4-*Chloro-3-nitrophenyl* n-*propyl ketone* was faintly odorous, and was sparingly soluble in light petroleum or cold alcohol, but dissolved more readily in ether.   On oxidation with aqueous chromic acid solution in presence of sulphuric acid, 4-chloro-3-nitrobenzoic acid (m. p. 180°) was obtained.

The *phenylhydrazone* separated from alcohol in acicular, golden yellow crystals melting at 116—117° (Found : $N = 12.91$. $C_{16}H_{16}O_2N_3Cl$ requires $N = 13.23$ per cent.).

The p-*nitrophenylhydrazone*, obtained as a bright yellow, crystalline powder, melted at 215° (Found : $N = 15.53$. $C_{16}H_{15}O_4N_4Cl$ requires $N = 15.45$ per cent.).

On heating 4-chloro-3-nitrophenyl n-propyl ketone with phosphoric acid at 150—160°, no evidence was obtained of the fission of the butyryl group, the bulk of the substance being recovered unchanged (compare Klages and Lickroth, *Ber.*, 1899, **32**, 1563), excepting for a trace of 3-*nitro-4-hydroxyphenyl* n-*propyl ketone* (XIV), which was obtained more readily on heating the nitrochloro-compound with eighty times its weight of 6 per cent. aqueous potassium hydroxide solution.   This nitrophenolic substance was obtained from boiling light petroleum in pale yellow needles melting at 46° (Found : $N = 6.71$. $C_{10}H_{11}O_4N$ requires $N = 6.70$ per cent.);   it was readily soluble in the ordinary organic solvents with the exception of light petroleum.

The p-*nitrophenylhydrazone*, separating from glacial acetic acid in masses of orange crystals, melted at 203—204° (Found : $N = 16.50$. $C_{16}H_{16}O_5N_4$ requires $N = 16.27$ per cent.).

4-*Chloro-3-aminophenyl* n-*propyl ketone* (XI), obtained in good yield by the reduction of the corresponding nitro-compound in alcoholic solution with zinc dust and a trace of ammonium chloride, crystallised from alcohol or warm light petroleum in white, shining plates melting at 97° (Found : $N = 7.37$. $C_{10}H_{12}ONCl$ requires $N = 7.09$ per cent.).

The *hydrochloride* separated from warm dilute hydrochloric acid in colourless needles, sparingly soluble in water (Found : $HCl = 15.23$. $C_{10}H_{12}ONCl,HCl$ requires $HCl = 15.58$ per cent.).

The diazo-solution from the foregoing hydrochloride, when poured into alkaline β-naphthol, yielded the red *azo-β-naphthol*, which crystallised from glacial acetic acid in red, prismatic needles having a green reflex (m. p. 153°) and developed a reddish-purple coloration with concentrated sulphuric acid (Found : $N = 8.16$. $C_{20}H_{17}O_2N_2Cl$ requires $N = 7.94$ per cent.).

3 : 4-*Dichlorophenyl* n-*propyl ketone* (XV), prepared from 4-chloro-3-aminophenyl *n*-propyl ketone by the Sandmeyer reaction, was isolated by distillation in steam and obtained as a colourless oil which could not be induced to crystallise. The odour of this compound was faintly reminiscent of anise and resembled that of 4-chlorophenyl *n*-propyl ketone, although not so intense. 3 : 4-Dichlorophenyl *n*-propyl ketone was characterised by its p-*nitrophenylhydrazone*, which separated from warm glacial acetic acid in bright yellow, prismatic needles melting at 183° (Found : N = 12·10. $C_{16}H_{15}O_2N_3Cl_2$ requires N = 11·94 per cent.).

III. m - 4 - *X y l y l* n - *P r o p y l K e t o n e* (XVI).

The following method of preparation gave a better yield of the ketone than that obtained by previous workers (Claus, *J. pr. Chem.*, 1891, [ii], **43**, 532; Klages, *Ber.*, 1902, **35**, 2257).

A small quantity of *n*-butyryl chloride was added to a mixture of *m*-xylene (34·6 grams) and aluminium chloride (27 grams). After the mixture had been warmed to 60° and an evolution of hydrogen chloride had commenced, further amounts of the acyl chloride were gradually added, the temperature being maintained at 50—60°. When all the *n*-butyryl chloride, amounting to 21·7 grams, had been added, the reaction was allowed to proceed at 50—60° with constant agitation for three hours, then at the ordinary temperature for a period of twelve hours and finally at 60° for three hours. The product, after being poured into water and washed with dilute sodium hydroxide solution, was dried and fractionally distilled. A fraction amounting to 26·25 grams was collected between 252° and 259°, and on repeated fractionation 23 grams of pure *m*-4-xylyl *n*-propyl ketone were obtained boiling at 258—259°/760 mm.; 9·95 grams of *m*-xylene were recovered, the yield of pure ketone amounting to 64 per cent. of the theoretical. *m*-4-Xylyl *n*-propyl ketone gave a p-*nitrophenylhydrazone*, which separated from alcohol in small, bright yellow crystals melting at 102—103° (Found : N = 13·79. $C_{18}H_{21}O_2N_3$ requires N = 13·50 per cent.).

6-*Nitro*-m-4-*xylyl* n-*Propyl Ketone* (XVII).—The introduction of one nitro-group into *m*-4-xylyl *n*-propyl ketone was effected by dissolving the ketone (8·8 grams) in twelve times its weight of concentrated sulphuric acid and, after cooling to 0°, adding slowly a mixture of 4·5 grams of nitric acid (*d* 1·42) and 36 grams of concentrated sulphuric acid. During the nitration the temperature was kept below 15° and the mixture stirred continuously for about two hours after all the nitric acid had been added. It was then

poured on to crushed ice. The precipitated, semi-solid product was removed, and after it had been cooled to $-10°$ and filtered at a low temperature there remained an almost white solid, which was washed successively with dilute sodium carbonate solution and water. It crystallised from warm alcohol in masses of slender, bayonet-shaped needles melting at 59—60° (Found : C = 65·2; H = 6·66 ; N = 6·43. $C_{12}H_{15}O_3N$ requires C = 65·13 ; H = 6·83 ; N = 6·33 per cent.).

6-*Nitro*-m-4-*xylyl* n-*propyl ketone* was only moderately soluble in cold alcohol, but more readily so in chloroform, light petroleum, or glacial acetic acid. On oxidation with an aqueous solution of chromic acid in presence of dilute sulphuric acid, 5-nitro-2 : 4. dimethylbenzoic acid was obtained, melting at 194—195° (Claus, *J. pr. Chem.*, 1890, [ii], **41**, 495, gives m. p. 195° [uncorr.]; Ahrens, *Annalen*, 1892, **271**, 18, gives m. p. 196—197°).

2-*Nitro*-m-4-*xylyl* n-*Propyl Ketone* (XIX).—The liquid product of the nitration, after being washed with sodium carbonate solution and water, deposited appreciable amounts of the 6-nitro-compound when cooled to $-15°$, and further quantities of the solid isomeride were removed by extracting the oily portion with small quantities of alcohol. After a prolonged treatment with alcohol at temperatures below 0°, an oil was obtained which did not solidify at $-15°$ (Found : N = 6·42. $C_{12}H_{15}O_3N$ requires N = 6·33 per cent.). The oil, however, was not pure, for on oxidation a mixture of nitrodimethylbenzoic acids was obtained.

6-*Amino*-m-4-*xylyl* n-*propyl ketone* (XVIII), obtained by the reduction of the nitro-compound with zinc dust and ammonium chloride in alcoholic solution, separated from warm light petroleum in hard, almost colourless, hexagonal prismatic needles melting at 56° (Found : N = 7·44. $C_{12}H_{17}ON$ requires N = 7·33 per cent.). The *hydrochloride* crystallised from warm dilute hydrochloric acid in white, slender, acicular crystals (Found : Cl = 15·61. $C_{12}H_{17}ON,HCl$ requires Cl = 15·58 per cent.). The *sulphate* separated from water in long, fern-like crystals.

Acetylation with acetic anhydride yielded 6-*acetylamino*-m-4-*xylyl* n-*propyl ketone*, crystallising from petroleum (b. p. 80—100°) in a white, tangled mass of needles melting at 123° (Found : N = 6·35. $C_{14}H_{19}O_2N$ requires N = 6·01 per cent.). This amine, diazotised in dilute hydrochloric acid and coupled with alkaline β-naphthol, gave *butyro-*2 : 4-*dimethylphenone-5-azo-β-naphthol*, which crystallised from warm glacial acetic acid in bright red masses of slender needles and had a faint, green reflex (m. p. 194—195°) (Found : N = 8·44. $C_{22}H_{22}O_2N_2$ requires N = 8·09 per cent.). The azo-derivative was sparingly soluble in cold alcohol or

glacial acetic acid, but dissolved more readily in chloroform; it dissolved in concentrated sulphuric acid to a reddish-purple solution.

6-*Chloro*-m-4-*xylyl* n-*Propyl Ketone* (XXI).—The replacement of the amino-group by chlorine was effected by the Sandmeyer reaction. This chloro-derivative was obtained by distillation in steam as an almost colourless oil, solidifying on cooling to 0°. Two crystallisations from alcohol at temperatures below 0° furnished a white, crystalline powder melting at 9—10° (Found: Cl = 16·44. $C_{12}H_{15}OCl$ requires Cl = 16·83 per cent.). This substance had a characteristic odour similar to that of honey, but not so powerful as that of 4-chlorophenyl n-propyl ketone.

Oxidation with chromic acid solution gave an acid which crystallised from alcohol in small, white needles melting at 165° after one crystallisation. This acid is presumably 5-*chloro*-2 : 4-*dimethylbenzoic acid*, which does not appear to have been previously described.

2 : 6-*Dinitro*-m-4-*xylyl* n-*Propyl Ketone* (XX).—m-4-Xylyl n-propyl ketone (1 gram) was nitrated by adding its solution in 9 grams of concentrated sulphuric acid to a mixture of 10·5 grams of nitric acid (d 1·5; free from nitrous acid) and 27 grams of sulphuric acid, cooled to −12°, and stirred continuously. On pouring on to ice, a milky, semi-solid mass separated, which was taken up with ether and washed successively with sodium carbonate solution, dilute sodium hydroxide, and water. Evaporation of the solvent gave 2 : 6-*dinitro*-m-4-*xylyl* n-*propyl ketone* as a pale yellow oil which solidified after two or three weeks; it separated from alcohol in a mass of white, hair-like needles melting at 63° (Found: N = 10·78. $C_{12}H_{14}O_5N_2$ requires N = 10·52 per cent.).

IV. p - *D i b u t y l b e n z e n e* (XXII).

p-*Di*-n-*butylbenzene* was prepared by the action of sodium on a mixture of p-dichlorobenzene and n-butyl chloride. The yield, however, was small, and the numerous by-products obtained added to the difficulty of isolating the hydrocarbon in a pure state.

The reaction was carried out in a capacious flask immersed in an oil-bath, heated to 110° and subsequently to 150°. n-Butyl chloride (72 grams) and p-dichlorobenzene (60 grams) dissolved in 50 c.c. of xylene were gradually added to 50 grams of sodium shavings covered with xylene (75 c.c.), so that the heat of the reaction was just sufficient to keep the solvent boiling. The product was filtered to remove sodium and sodium chloride, and the cake of mineral matter was extracted thoroughly with warm benzene. After the bulk of the solvent had been removed from the combined extract

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and washings, a dark brown, viscous residue remained, having a
faintly green appearance in reflected light. The product was
distilled, fractions being collected up to 280—300°. By means
of a lengthy process of fractionation, followed by treatment with
metallic sodium, p-*di*-n-*butylbenzene* was obtained boiling at
224—225·5°/759 mm. (Found : C = 88·75, 88·76; H = 10·95,
11·30. $C_{14}H_{22}$ requires C = 88·34; H = 11·66 per cent.). After
further distillations, the hydrocarbon gave C = 88·65; H = 11·3
per cent. Appreciable quantities of diphenyl were obtained in the
reaction, and no doubt the presence of traces of diphenyl accounts
for the high carbon content of the hydrocarbon. p-*Di*-n-*butyl*-
benzene is a colourless liquid having a faint, agreeable, orange-like
odour.

2-*Nitro*-1 : 4-*di*-n-*butylbenzene*.—Dibutylbenzene (7 grams) was
cooled to 0° and fuming nitric acid added in small quantities until
20 grams had been used. At the commencement of the operation
the acid layer became dark red. The hydrocarbon on the other
hand darkened as the nitration proceeded, until it was almost indis-
tinguishable from the lower stratum. The nitration was checked
as soon as nitrous fumes were evolved and the upper layer became
lighter in colour. The crude nitro-compound was separated and
treated repeatedly with water and sodium hydroxide solution until
the washings were not tinted red. It was purified by distillation in
steam, when 2-*nitro*-1 : 4-*di*-n-*butylbenzene* was obtained as a pale
yellow, refractive liquid, having a pleasant and characteristic odour,
faintly resembling that of lemons. It was purified for analysis by
further distillation in steam, the first and the last portions of the
distillate being rejected (Found : N = 6·14. $C_{14}H_{21}O_2N$ requires
N = 5·95 per cent.).

2-*Amino*-1 : 4-*di*-n-*butylbenzene* (XXIII).—The reduction of 2-
nitro-1 : 4-dibutylbenzene to the corresponding amino-compound
did not proceed smoothly when zinc dust and ammonium chloride,
or tin or zinc with aqueous or alcoholic hydrochloric acid were
employed as reducing agents. More favourable results were
obtained by the use of iron filings and acetic acid, but even under
these conditions the product was contaminated with appreciable
quantities of a less basic substance.

The nitro-compound (6·4 grams), dissolved in 15 c.c. of glacial
acetic acid, was gradually added to 15 grams of iron filings covered
with 50 grams of 80 per cent. acetic acid. The mixture was gently
heated during the addition of the nitrodibutylbenzene and for a
period of one hour after all the nitro-compound had been added.
The bulk of the acetic acid was removed by distillation, and the crude
amine isolated by distillation in steam after making the residue

alkaline. It was partly purified by conversion into the sparingly soluble *sulphate*, which was extracted with ether. From the sulphate a moderately pure specimen of the base was obtained as a colourless liquid having a faint yet characteristic odour somewhat resembling that of mushrooms. The *hydrochloride*, which is soluble in water or chloroform, separated from dilute hydrochloric acid in white, flattened needles.

2-Benzoylamino-1 : 4-*di*-n-*butylbenzene*, after repeated crystallisation from alcohol, separated in white masses of needles melting at 116° (Found : C = 81·4; H = 8·6. $C_{21}H_{27}ON$ requires C = 81·5; H = 8·8 per cent.).

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THE CHEMICAL DEPARTMENT,
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Organic Chemistry.

Preparation of Ethylene by Hydrogenation of Acetylene.
WILLIAM H. ROSS, JAMES B. CULBERTSON, and J. P. PARSONS
(*J. Ind. Eng. Chem.*, 1921, **13**, 775—778).—Metallic nickel, prepared
by reducing the oxide at 300°, has a greater capacity than has
coconut charcoal for adsorbing hydrogen at the ordinary tempera-
ture. When a mixture of equal volumes of hydrogen and acetylene
is passed into a tube, from which the air is exhausted, about one-
third filled with freshly-reduced nickel, the hydrogen adsorbed by
the nickel, together with that added, may be sufficient to convert
the acetylene completely into ethane. If the tube is then exhausted
and the mixture of hydrogen and acetylene introduced until the
excess of hydrogen is used up, a product may be obtained which
contains more than 80% of ethylene. The best results are obtained
when the mixture contains a slight excess of hydrogen, but as this
is further increased, the amount of ethylene decreases and the
quantity of ethane increases correspondingly. The adsorbed
hydrogen in an active nickel catalyst may be eliminated by repeated
treatment with acetylene; whilst the nickel does not lose its activity,
it is then without action on either ethylene or acetylene. W. P. S.

Unsaturation and Molecular Compound Formation. II.
O. MAASS and J. RUSSELL (*J. Amer. Chem. Soc.*, 1921, **43**, 1227—
1230; cf. A., 1918, i, 534).—Freezing-point determinations have
been made for the system allylene–hydrogen bromide, and from
these it is shown that two eutectics and one molecular compounds
exist. The eutectics lie at −132° and −138° respectively, and the
molecular compound, C_3H_4,HBr, melts at −126°. The behaviour
of allylene in forming a molecular compound differs from that of
acetylene, but this difference is the same as was observed in the
case of benzene and substituted benzenes, and confirms the authors'
view that the formation of an atomic compound is always preceded
by the formation of a molecular compound (*loc. cit.*). Exact
details are given of a method, based on that of Lebeau and Pichon
(A., 1913, i, 438), for the preparation of large quantities of pure
allylene. The pure substance melts at −105·0° and boils at −27·0°.
Under ideal conditions, the value 40 is found for the molecular
weight. J. F. S.

**Molecular Rearrangement of Unsaturated Compounds in
Acid Solution.** ALF. GILLET (*Bull. Soc. chim. Belg.*, 1921, **30**,
226—252).—The general rules already enunciated (this vol., i, 533)
are illustrated by numerous examples. The opening of a tri-
methylene ring by addition of water or acids conforms with the rules
referred to. Examples of the converse reaction are lacking, but the
compound $CH_2:CMe\cdot CMe:CH_2$, which is the "normal" product of
dehydration of pinacone, may be expected, owing to the negative

character of the CH_2 groups and the positive character of the intermediate groups, to undergo transformation into the following compounds in acid solutions : $CH_2<^{CMe}_{CMe}>CH_2 \rightarrow OH \cdot CMe<^{CMe_2}_{CH_2}$
$\rightarrow O\!:\!CMe \cdot CMe_3$ (pinacolin). This explains the mechanism of the various transformations undergone by the pinacones and analogous compounds, numerous examples of which are cited and classified. The various types of " ethylenic transformations " (*loc. cit.*), such as shifting of the double bond, addition or subtraction of water or acids, and keto-enol rearrangements, and the mechanism of the dehydration of alcohols, are discussed from the point of view of the general rules. Many of these cases are explained very simply, but for others the intermediate formation and rupture of one or two trimethylene rings is assumed. The type of transformation in any case depends chiefly on the constitution of the compound and the electro-positive or -negative character of the radicles present. The catalyst as a rule plays a very subordinate part in determining the character of the reaction.   J. H. L.

Preparation of Alkyl Vinyl Ethers and their Homologues. PLAUSONS FORSCHUNGSINSTITUT G. M. B. H. (D.R.-P. 338281; from *Chem. Zentr.*, 1921, iv, 421. See also Plauson and Vielle, Brit. Pat. 156121).—Homologues of alkyl vinyl ethers are prepared by replacement of the C_2H_2 group by homologous groups. *Ethyl vinyl ether*, b. p. 35°/760 mm., is decomposed by sulphuric acid.
                          G. W. R.

The Molecular Conductivity of some Sulphonium Compounds in Acetone. SIR PRAPHULLA CHANDRA RÂY and KALI-KUMAR KUMAR (T., 1921, **119**, 1643—1644).

Decomposition of Ethyl Thioacetate by Mercury Salts; a Contribution to the Chemistry of Mercury Mercaptides. GEORG SACHS (*Ber.*, 1921, **54**, [*B*], 1849—1854).—Ethyl thio-acetate is remarkably resistant towards solutions of alkali hydroxide by which it is hydrolysed slowly to ethyl mercaptan and acetic acid. It is therefore remarkable that a similar hydrolysis is immediately induced by the addition of an alcoholic solution of mercury acetate to the ester, ethylmercaptomercurichloride, $SEt \cdot HgCl$, being precipitated by the addition of water and sodium chloride to the product. It appears necessary in son e degree to use the mercury compound in the form of its acetate, since only a slow hydrolysis is observed with mercuric chloride solution, and it is suggested that the compound $SEt \cdot Hg \cdot OAc$ is initially formed and remains in solution. Evidence in favour of this hypothesis is adduced from the formation of the compound $C_4H_8O_2SHg$, microscopic rods, m. p. 140—146°, when solutions of ethyl thioacetate and mercuric acetate in acetic anhydride are mixed; by a modification of the conditions of this reaction it is found possible to isolate a second *compound*, $C_{12}H_{22}O_8S_2Hg_3$, m. p. 140—142°, to a turbid liquid, decomp. 144—146°, which is also produced from mercuric acetate and ethyl mercaptan in acetic anhydride solution. Prolonged agitation of

ethylmercaptomercurichloride with a saturated ethereal solution of mercuric chloride leads to the formation of the additive *compound*, $SEt \cdot HgCl, HgCl_2$, slender needles or prisms, m. p. 150° (decomp.).

H. W.

Experiments on the Synthesis of the Polyacetic Acids of Methane. III. Conditions Controlling Synthesis by the Cyanoacetic Ester Method—(*continued*). CHRISTOPHER KELK INGOLD and EDWARD ARTHUR PERREN (T., 1921, **119**, 1582—1601).

Solubilities of some Active and Racemic Tartrates and Malates. MARCEL DUBOUX and LÉON CUTTAT (*Helv. Chim. Acta*, 1921, **4**, 735—761).—A series of determinations carried out with the object of ascertaining whether the salts of inactive acids are invariably less soluble than those of the active forms. Of the compounds investigated, barium tartrate is the only exception to this rule. Analytical applications of this are referred to (Kling, A., 1910, ii, 359; Duboux, *Bull. Soc. Vaud. Sci. Nat.*, 1916, **51**, 55), and it is mentioned that calcium is better estimated in water as racemate than as oxalate, since magnesium does not then affect the results (Caeiro, *Diss.*, Lausanne, 1918).

The values given are in terms of grams of anhydrous salt per 100 grams of solution at temperatures of 0°, 12·5°, 25°, and 37·5°.

Tartrates. *Active.*—$MgA,4H_2O$, 0·540, 0·848, 1·174, 1·050; $CaA,4H_2O$, 0·0192, 0·0268, 0·0360, 0·0498; $SrA,4H_2O$, 0·0942, 0·1285, 0·1765, 0·2395; $BaA,\frac{1}{2}H_2O$, 0·0200, 0·0247, 0·0294, 0·0341; PbA, 0·0027, 0·0030, 0·0035, 0·0046.

Inactive.—$Mg_2A_2,10H_2O$, 0·403, 0·582, 0·826, 1·095; $Ca_2A_2,8H_2O$, 0·0023, 0·0034, 0·0045, 0·0056; $Sr_2A_2,8H_2O$, 0·0107, 0·0202, 0·0297, 0·0392; Ba_2A_2, 0·0243, 0·0284, 0·0325, 0·0366; $Pb_2A_2,4H_2O$, 0·0038, 0·0020, 0·0034, 0·0066.

Malates. *Active.*—$MgA,3H_2O$, 2·02, 2·28, 2·54, 2·80; $CaA,2H_2O$, 0·670, 0·805, 0·921, 1·011; $SrA,4H_2O$, 0·193, 0·332, 0·490, 0·781; BaA, 1·020, 1·150, 1·240, 1·310, $PbA,2H_2O$, 0·015, 0·027, 0·052, 0·089.

Inactive.—$Mg_2A_2,5H_2O$, 0·93, 1·08, 1·23, 1·38; $Ca_2A_2,3H_2O$, 0·244, 0·277, 0·310, 0·343; $Sr_2A_2,5H_2O$, 0·290, 0·325, 0·422, 0·550; Ba_2A_2,H_2O, 0·76, —, 0·58, 0·84; $Pb_2A_2,2H_2O$, 0·015, 0·023, 0·035, 0·0545.

Above 26·2°, active magnesium tartrate is dihydrated. J. K.

Ethylglycoloside as a Type of αβ-Glucosides. MAX BERGMANN and ARTUR MIEKELEY (*Ber.*, 1921, **54**, [*B*], 2150—2157).—The discovery of γ-methylglucoside, the behaviour of the rhamnosides, and the attribution of an ethylene oxide structure to the glucosidic oxygen bridge in lævulose, inulin, etc. (cf. Haworth and Law, T., 1916, **109**, 1324; Irvine and Steele, T., 1920, **107**, 1474), has increased the interest in this type of substance, and the authors have therefore prepared ethylglycoloside, $\begin{smallmatrix} CH_2 \\ O \end{smallmatrix} \!\!>\!\! CH \cdot OEt$, as a very simple member of the series. When dissolved in phenol at 30—40°, the substance

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is bimolecular, but unimolecular under greatly diminished pressure at 160°; the hypothesis that the action is of the type, $\overset{CH_2}{\underset{O}{|}}\!\!>\!\!CH\cdot OEt$ $\rightleftharpoons \overset{CH_2\cdot CH(OEt)\cdot O}{\underset{O-CH(OEt)-CH_2}{|\quad\quad\quad\quad|}}$, analogous to that assumed in the case of glycollaldehyde appears to be highly improbable. Its close relationship to ethylene oxide renders it less stable than the usual α- and β-glucosides; it is scarcely affected by water, and hence does not reduce Fehling's solution, even at the boiling point, but, on the other hand, it is exceedingly sensitive to acids, being rapidly hydrolysed to a certain extent by boiling $N/1000$-hydrochloric acid. When treated with phenylhydrazine hydrochloride and sodium acetate, it gives a somewhat considerable amount of glyoxalosazone, the effect being due to the presence of free acetic acid. This property is shared by other non-furoid glucosides, for example γ-methylrhamnoside. In this connexion, it is pointed out that sucrose is not so indifferent towards the phenylhydrazine mixture as is generally supposed. In general, the osazone test does not seem well adapted in every case for distinguishing between glucoside and free sugar.
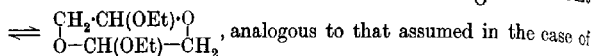
Ethylglycoloside, m. p. 59—60°, after softening at 58°, b. p. 90°/12 mm., 122°/51 mm., is prepared by the action of perbenzoic acid on a well-cooled solution of ethyl vinyl ether in absolute ether; it has $d_4^{21\cdot5}$ 1·0436, d_4^{24} 1·0428, n_D^{20} 1·4293. It is converted by an alcoholic solution of hydrogen chloride into glycollaldehyde acetal.

The authors proposed to designate glucosides of known structure by adding to their names two figures denoting the points of attachment of the glucosidic oxygen bridge, the enumeration, as in the case of dextrose, to commence with the aldehydic carbon atom, for example, methylglucoside-(αδ), ethylglycoloside-(αβ); ε-glucosido-(αδ)-mannose.   H. W.

Mytilitol, a Naturally Occurring Cyclose. D. ACKERMANN (*Ber.*, 1921, **54**, [*B*], 1938—1943).—The isolation of mytilitol from *Mytilus edulis* is described in detail. It forms colourless, lustrous crystals, m. p. 259°, is optically inactive, and does not contain a methoxyl group. It is converted by acetic anhydride into a *penta-acetate*, microscopic needles, m. p. 157—158°, and by acetic anhydride and concentrated sulphuric acid into the *hexa-acetate*, m. p. 180—181°. The parent substance is therefore regarded as methyl*cyclo*hexanehexol. It has been examined previously by Jansen (A., 1913, i, 791), who regarded it as *cyclo*hexanepentol. It is difficult to decide between the two conceptions on the basis of analyses of the parent substance and of its derivatives, but the percentage of water of crystallisation in hydrated mytilitol and the values for carbon in the anhydrous substance harmonise better with the present formula, which is further supported by the insolubility of mytilitol in organic solvents and its sparing solubility in cold water; it is scarcely conceivable that an isomeride of quercitol would exhibit these properties.   H. W.

Optical Rotation of Dextrose under the Influence of Hydrochloric Acid. II. The Change of Rotatory Power and Reducing Capacity of Dextrose Solutions in Hydrochloric Acid at 100°. HANS MURSCHHAUSER (*Biochem. Zeitsch.*, 1921, **116**, 171—190; cf. A., 1920, i, 661).—The optical activity and reducing capacity of 20, 10, 5, and $2\frac{1}{2}\%$ dextrose solutions in 5·1, 8·1, and 10·1% hydrochloric acid solutions were determined over a period of twelve hours at 100°. In general, the behaviour of both properties in the first two hours shows considerable variation, but afterwards the fall in rotation and reducing power is a linear function of the time, and the greater the concentration of the acid the greater the effect produced. For 10 and 20% dextrose solutions, a maximum of optical rotation is attained in the first two hours, due, probably, to the formation of *iso*maltose. H. K.

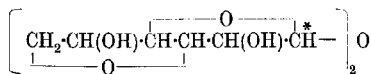**Polysaccharides. X. Anhydro-sugars of the Trehalose Type : Diglucan and *iso*Diglucan.** P. KARRER, FR. WIDMER, and ALEX. P. SMIRNOV (*Helv. Chim. Acta*, 1921, **4**, 796—801).— By the action of silver carbonate on a suspension of acetodibromoglucose in chloroform, ζ-bromo-βγε-triacetylglucose is produced, with a small proportion of two forms of ζζ′-dibromo-βγεβ′γ′ε′-hexacetyl-α-glucosidoglucose (I), neither of which reduces Fehling's solution until hydrolysed by acid.

$$\left[CH_2Br\cdot CH(OAc)\cdot CH\cdot CH(OAc)\cdot CH(OAc)\cdot CH\right]_2O.$$
$$\underbrace{\qquad\qquad O\qquad\qquad}$$
$$(I.)$$
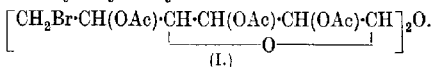
The α-*form*, m. p. 212°, is optically inactive and much less soluble in alcohol than the β-form, needles, m. p. 152°, $[\alpha]_D$ −10·2°. The exact relationship of these compounds to the trehaloses remains undecided. Both are converted by boiling barium hydroxide solution into dianhydrodisaccharides, $C_{12}H_{18}O_9$. *Diglucan*, from the α-form, hexagonal polyhedra, m. p. 170—175°, $[\alpha]_D^{17}$ −214·1°, is easily soluble in water. iso*Diglucan*, from the β-form, has not been crystallised, is lævorotatory, more readily soluble than diglucan in alcohol, and, like this, only reduces Fehling's solution after hydrolysis. They differ by the configurations of the asterisked carbon atoms in the formula

$$\left[CH_2\cdot CH(OH)\cdot \overset{\displaystyle|}{CH}\cdot CH\cdot CH(OH)\cdot \overset{*}{CH}-\right] O$$
$$\underbrace{\qquad O\qquad} \qquad\qquad\quad {}_2$$

J. K.

Polysaccharides. XI. Compounds of Anhydro-sugars with Alkali Hydroxides. A Method of Determining the Parent Compound of Polymeric Anhydro-sugars. P. KARRER (*Helv. Chim. Acta*, 1921, **4**, 811—820).—Solutions of di-, α-tetra-, β-hexa-, and α-octa-amyloses in dilute aqueous sodium hydroxide contain additive compounds, which are precipitated by alcohol, and after purification by solution and reprecipitation, respectively correspond exactly with the formulæ $C_{12}H_{20}O_{10}$,NaOH, $(C_{12}H_{20}O_{10}$,NaOH$)_2$, $(C_{12}H_{20}O_{10}$,NaOH$)_3$, and $(C_{12}H_{20}O_{10}$,NaOH$)_4$.

Polymeric anhydro-sugars, as internal acetals, therefore combine with one molecule of sodium hydroxide per molecule of anhydro-sugar, and so permit the determination of the molecular weight of this. Thus β-hexa-amylose is a polymeric maltose anhydride (cf. this vol., i, 768), inulin is probably derived from anhydro-difructose (cf. Pfeiffer and Tollens, A., 1882, 490), and xylan from anhydro-dixylose (cf. Abderhalden, *Biochem. Handlex.*, ii, 32). In further confirmation of previous results, a *compound*, $(C_{12}H_{20}O_{10},NaOH)_2$, was obtained from soluble starch. It is suggested that such poly-saccharides are crystalline substances, of which the lattice points are occupied by polymeric molecules, which in the case of starch are diamylose complexes, $(C_{12}H_{20}O_{10})_2$ or $(C_{12}H_{20}O_{10})_3$. The forces of valency by which the polymeric molecules are fixed in the crystal are so strong that the resulting " crystal-polymerisation " very closely resembles true polymerisation. If the forces in question approximate in strength to those responsible for the existence of the polymerides, and also to those operating in the anhydro-sugar, it will be extremely difficult to isolate intermediate degradation products. This is probably the case with cellulose.   J. K.

A New Method for the Preparation of Anhydro-sugars. P. KARRER and ALEX. P. SMIRNOV (*Helv. Chim. Acta*, 1921, 4, 817—820).—Acetobromoglucose combines with trimethylamine in alcoholic solution to form *tetracetylglucosidotrimethylammonium bromide*, $C_{17}H_{28}O_9NBr$, well-defined polyhedra of neutral reaction, m. p. 192°, $[\alpha]_D^{18}+10\cdot2°$, which is quantitatively converted into lævoglucosan by warming its aqueous solution for a short time with an alkali or alkaline earth hydroxide. Since this reaction is a form of the Hofmann degradation of quaternary ammonium hydroxides, and yet, if the current formula for lævoglucosan be accepted, results in ring formation, it is suggested that caution is necessary in deriving constitutional formulæ from such reactions.
    J. K.

Polymerisation of Glucosan. AMÉ PICTET and JACQUES PICTET (*Helv. Chim. Acta*, 1921, 4, 788—795).—Glucosan, like lævoglucosan (A., 1899, i, 527), may be polymerised by means of platinum black, but the change in each case is more conveniently effected with the aid of a trace of anhydrous zinc chloride. The product obtained from glucosan varies with the conditions employed. *Diglucosan*, $(C_6H_{10}O_5)_2$, m. p. 160° (decomp.), $[\alpha]_D +54\cdot5°$ (*tetrabenzoate*, $C_{40}H_{36}O_{14}$, m. p. 128—129°), is produced at 155°/15 mm., is easily soluble in water, has a sweet taste, does not react with phenylhydrazine, and is hydrolysed by mineral and oxalic acids, but not by water. This is expressed by the formula (I). *Tetraglucosan*, $(C_6H_{10}O_5)_4,2H_2O$, $[\alpha]_D +82\cdot76°$ (*octa-acetate*, $C_{40}H_{58}O_{28}$, m. p. 84—85°; *octabenzoate*, $C_{80}H_{72}O_{28}$, m. p. 109—110°), is not completely dehydrated at 110°, and resembles the dextrins, especially those derived from lævoglucosan, in properties. It does not react with phenylhydrazine, but does so very slightly with Fehling's solution after prolonged boiling. Its mode of formation is probably similar to that of diglucosan,

and it is also produced from dextrose and zinc chloride at 180° under ordinary pressure. Tetralævoglucosan, from lævoglucosan and zinc chloride at 155°, appears to be to some extent depolymerised to lævoglucosan by distillation under reduced pressure. The rotatory power ($[\alpha]_D + 73\cdot85$) and molecular weight of the product of polymerisation of equal proportions of glucosan and lævoglucosan at 155° under ordinary pressure suggests the presence of a mixed polymeride, $(C_6H_{10}O_5)_4$, with those derived from the separate substances. No definite results were obtained from attempts by hydrolysis of these polymerides to secure partial degradation to disaccharides.

$$\underset{(\mathrm{I.})}{\overset{\begin{array}{c}\overset{\lceil\ \ \ \ -\mathrm{O}-\ -\ \rceil}{\mathrm{CH\cdot CH\cdot CH(OH)\cdot CH\cdot CH(OH)\cdot CH_2\cdot OH}}\\ \mathrm{O\ \ \ O}\end{array}}{\underset{\lfloor\ -\ -\mathrm{O}-\ -\ \rfloor}{\mathrm{OH\cdot CH_2\cdot CH(OH)\cdot CH\cdot CH(OH)\cdot CH-CH}}}}$$

<div style="text-align:right">J. K.</div>
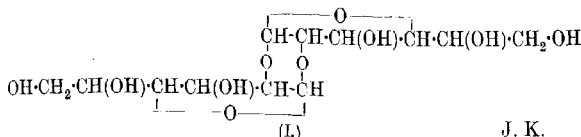
Constitution of the Sugar-acetones. P. KARRER and O. HURWITZ (*Helv. Chim. Acta*, 1921, **4**, 728—734).—Glycerolacetone is attacked by alkaline permanganate at 20°, but glucose- and fructose-diacetones are almost quantitatively recovered after prolonged warming with this reagent. It is therefore concluded that both the terminal carbon atoms of the sugars are in each case involved in the condensation with acetone, the secondary alcoholic groups being sterically protected from oxidation. Similarly, lævoglucosan is almost unattacked (Vongerichten and Müller, A., 1906, i, 198; Pictet and Cramer, A., 1920, i, 819), whilst glucosan and lævulosan suffer immediate oxidation (cf. this vol., i, 544). The formula (I) is therefore proposed in preference to that of Irvine and Scott (T., 1909, **95**, 1220) for glucosediacetone, and equally explains its reactions (Irvine and Scott, *loc. cit.*; Irvine and Paterson, T., 1914, **105**, 908). Fructosediacetone is written (II), the mode of attachment of the bridge oxygen atom explaining the identity of the osazones from the monomethyl-glucose and -fructose respectively obtained from glucose- and fructose-diacetones (Irvine and Scott, *loc. cit.*). Irvine and Paterson's formula for α-mannitoldiacetone, with a primary alcoholic group, is confirmed, whilst the β-isomeride (Fischer and Rund, A., 1916, i, 863) is only slightly attacked, although the fact that it contains two free hydroxyl groups as compared with one in the cases of glucose- and fructose-diacetones renders it less resistant. It is assigned the formula (III).

$$\underset{(\mathrm{I.})}{\begin{array}{c}\overset{\lceil\ -\ -\mathrm{O}-\ -\ \rceil}{\mathrm{CH\cdot CH\cdot CH(OH)\cdot CH\cdot CH\cdot CH_2}}\\ \mathrm{O\ \ \ O}\qquad\qquad\mathrm{O\ \ \ O}\\ \diagdown\diagup\qquad\qquad\diagdown\diagup\\ \mathrm{CMe_2}\qquad\qquad\mathrm{CMe_2}\end{array}}\qquad\underset{(\mathrm{II.})}{\begin{array}{c}\overset{\lceil\ -\ -\mathrm{O}-\ -\ \rceil}{\mathrm{CH_2\cdot C\cdot CH(OH)\cdot CH\cdot CH\cdot CH_2}}\\ \mathrm{O\ \ \ O}\qquad\qquad\mathrm{O\ \ \ O}\\ \diagdown\diagup\qquad\qquad\diagdown\diagup\\ \mathrm{CMe_2}\qquad\qquad\mathrm{CMe_2}\end{array}}$$

$$\underset{(\mathrm{III.})}{\begin{array}{c}\mathrm{CH_2\cdot CH\cdot CH(OH)\cdot CH(OH)\cdot CH\cdot CH_2}\\ \mathrm{O\ \ \ O}\qquad\qquad\mathrm{O\ \ \ O}\\ \diagdown\diagup\qquad\qquad\diagdown\diagup\\ \mathrm{CMe_2}\qquad\qquad\mathrm{CMe_2}\end{array}}$$
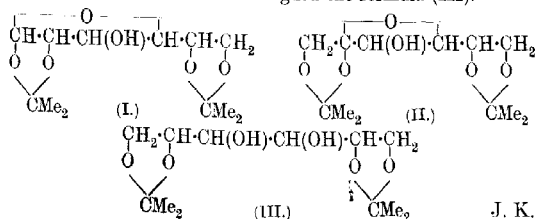
<div style="text-align:right">J. K.</div>

Starch. A. REYCHLER (*Bull. Soc. chim. Belg.*, 1921, **30**, 223–226; cf. this vol., i, 498).—Modifying an experiment described by Roux (A., 1905, i, 262), the author has isolated a reversion product from starch paste, after prolonged chilling. It is concluded that the reversion process concerns chiefly the parietal matter of the starch grain, and that this matter is very similar to the "artificial starch" or the "amylose" of Maquenne. The author reaffirms his earlier statement that each starch grain possesses two hila, one on each side of the grain.   J. H. L.

Starch. A. REYCHLER (*Bull. Soc. chim.*, 1921, [iv], **29**, 833–836; cf. this vol., i, 498).—As a result of further experimental work, the author concludes that the starch grain has a protective coating, which is very little acted on by cold water. It swells up, is distended, and more or less ruptured by boiling water. In a fresh starch paste, this material is easily liquefied by malt extracts, but if it has been kept for some days it is more refractory. It then resists the action of diastase and maintains its characteristic form, finally giving a deposit, in the form of a gel, which cannot be saccharified. It is soluble when heated with water at 140—150° under pressure, but on cooling the solution, it is deposited again in the form of artificial starch or Maquenne's pure amylose (cf. A., 1906, i, 327, 547).   W. G.

Polysaccharides. VIII. Starch and the Amyloses. P. KARRER, C. NÄGELI, O. HURWITZ, and A. WÄLTI (*Helv. Chim. Acta*, 1921, **4**, 678—699; cf. this vol., i, 397).—α-Tetra-amylose does not yield acetobromomaltose when treated with acetyl bromide in entire absence of water, but an amorphous product containing bromine, and resembling that obtained from starch under similar conditions. The least trace of acetic acid induces the formation of the same proportion of acetobromomaltose as is obtained from an equal weight of maltose, a small amount of acetobromoglucose being also produced if the temperature be not maintained sufficiently low, for example below 10° for a trace of acetic acid. Air-dried soluble starch furnishes the same weight of acetobromomaltose as an equal quantity of maltose. Hence starch is a polymeride of anhydromaltose in which the glucose residues are not united by "glucoside-linkings." Further, acetylated starch, like acetylated triamylose, does not furnish bromo-compounds when treated with acetyl bromide, so that the opening of the anhydro-rings of starch by this reagent is due to hydrobromic acid. From dry β-hexa-amylose, however, a product is obtained very similar to, if not identical with, that derived from starch, whilst in presence of acetic acid the same proportion of acetobromomaltose is produced as from maltose. Hence β-hexa-amylose represents a polymeric form of maltose anhydride, isomeric with the α-amyloses.

Cold concentrated aqueous solutions of tetra-amylose give a blue colour with iodine, which disappears on warming, but reappears on cooling, like that of starch, but differs from this in that it is produced only in concentrated solution. Octa-amylose gives blue needles of an additive product, which is similarly affected by heat.

The α-amyloses, like starch, are converted into lævoglucosan by distillation in a vacuum, and also furnish potassium and sodium salts (cf. Pfeiffer and Tollens, A., 1882, 490). Octa- and β-hexa-amyloses are easily soluble in dilute sodium hydroxide solution.

A further analogy between starch and the amyloses follows from their behaviour towards pancreas-diastase, which ferments di- and α-tetra-amylose to maltose to the extent of 10% (cf. Pringsheim, A., 1913, i, 1281), although β-hexa- and α-octa-amyloses are unaffected. Intestinal ferments of the snail do not attack α-tetra-amylose or methylated starches. Lævoglucosan furnishes aceto-bromoglucose when treated with a solution of hydrogen bromide in glacial acetic acid, owing to acetylation of hydroxyl groups produced by breaking down of the anhydro-oxygen linking. Hence the position of this in the α-amyloses cannot be determined by subjecting them to this reaction (this vol., i, 313).
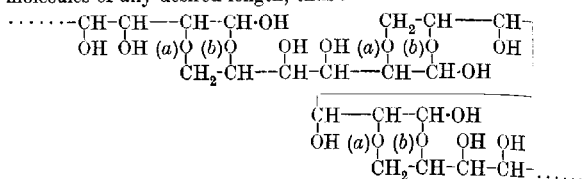
The respective heats of combustion of 1 gram of anhydrous maltose, diamylose, α-tetra-amylose, β-hexa-amylose, α-octa-amylose, starch, and lævoglucosan are 3949, 4235, 4186, 4165, 4610, 4183, and 4186 calories. Hence α-octa-amylose, which has a larger heat of combustion than any other known carbohydrate, and so is produced during fermentation of starch by *Bacillus macerans* in greater quantity at 47° than at 32°, probably represents the most highly polymerised form of α-amylose possible. Further, starch itself cannot be more highly polymerised, and so is doubtless a member of a series of polymerisation products of maltose anhydride isomeric with the α-amyloses, and corresponding probably with α-tetra-amylose, $(C_{12}H_{20}O_{10})_2$, or β-hexa-amylose, $(C_{12}H_{20}O_{10})_3$. Although no direct proof of this can yet be supplied, it agrees with molecular-weight determinations of methylo-starches (this vol., i, 311) and of soluble starch (Beckmann and Maxim, A., 1915, ii, 222) and with the fact that, like those of starch (Lintner, A., 1888, 497; Asboth, A., 1887, 868) solutions of octa-amylose, and, in presence of alcohol, of β-hexa- and α-tetra-amyloses yield precipitates with barium hydroxide. The composition of these varies somewhat with circumstances, although those from natural and soluble starches agree fairly closely in composition with those obtained from α-tetra- and β-hexa-amyloses under similar conditions. Further, the heat of combustion of starch exceeds 4163 calories, which is calculated as the maximum possible for a compound composed of a continuous chain of glucose residues, but agrees closely with the values for the anhydro-sugars lævoglucosan and α-tetra-amylose. The fact that the same applies to cellulose (4180 calories) is considered as evidence that this also has an anhydro-formula. Methylated wheat starch (M 1060), rice starch (M 844), and maize starch are described. J. K.
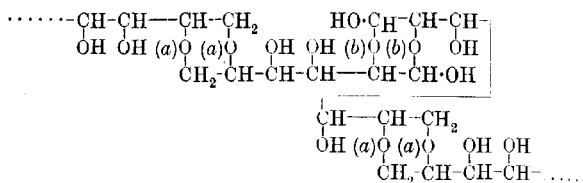
The Constitution of Cellulose and Cellobiose. ASTRID CLEVE VON EULER (*Chem. Zeit.*, 1921, **45**, 977—978, 998).—The important facts which must be taken into account in any structural formula assigned to cellulose are outlined and the directions in which all structural formulæ hitherto proposed for cellulose are

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unsatisfactory are indicated. It is possible, however, to conceive a formula for cellulose which is in agreement with its constitution as a high molecular condensation product, and may be reconciled with the properties of its derivatives and fission products. Two variations of a new formula for cellulose are proposed which contain the p-dioxan ring of Green's formula (A., 1905, i, 22), but have the advantage over the latter that they contain a chain of hexose molecules of any desired length, thus:

$$\cdots\cdots\text{-CH-CH---CH--CH-OH} \qquad \text{CH}_2\text{-CH----CH-}$$
$$\text{OH} \quad \text{OH} \ (a)\text{O} \ (b)\text{O} \qquad \text{OH} \ \text{OH} \ (a)\text{O} \ (b)\text{O} \qquad \text{OH}$$
$$\text{CH}_2\text{-CH---CH-CH----CH-CH-OH}$$

$$\text{CH----CH-CH-OH}$$
$$\text{OH} \ (a)\text{O} \ (b)\text{O} \quad \text{OH} \ \text{OH}$$
$$\text{CH}_2\text{-CH-CH-CH-}\ldots\ldots$$

(I.)

$$\cdots\cdots\text{-CH-CH---CH--CH}_2 \qquad \text{HO·CH-CH-CH-}$$
$$\text{OH} \quad \text{OH} \ (a)\text{O} \ (a)\text{O} \qquad \text{OH} \ \text{OH} \ (b)\text{O} \ (b)\text{O} \qquad \text{OH}$$
$$\text{CH}_2\text{-CH-CH-CH---CH-CH·OH}$$

$$\text{CH----CH--CH}_2$$
$$\text{OH} \ (a)\text{O} \ (a)\text{O} \quad \text{OH} \ \text{OH}$$
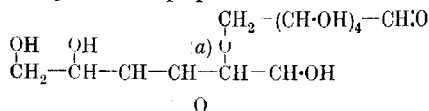$$\text{CH}_2\text{-CH-CH-CH-}\ \ldots\ldots$$

(II.)

The connecting oxygen atoms are of two kinds and are distinguished in the formulæ as (a) and (b). The combination (a) represents an ordinary anhydride (ether) linking which on the addition of the elements of water reacts thus:

$$\text{:CH·O·CH}_2 + \text{H}_2\text{O} = \text{:CH·OH} + \text{·CH}_2\text{·OH}.$$
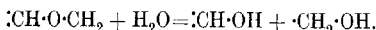
In combination (b), on the other hand, the oxygen is in a semi-acetal combination, and fission of the linking is accompanied by activation of the carbonyl oxygen without alteration in the gross formula. The elements of water are added first and then removed from the intermediate carbonyl hydrate, so that the nett result is:

$$\text{:CH·O·CH·OH} \longrightarrow \text{:CH·OH} + \text{·CH:O}$$
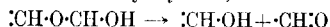
Arguments are adduced in favour of these formulæ for cellulose and the following formula is proposed for cellobiose:

$$\text{CH}_2 \text{-(CH·OH)}_4\text{--CH:O}$$
$$\text{OH} \quad \text{OH} \qquad \quad a)\ \text{O}$$
$$\text{CH}_2\text{--CH--CH---CH---CH - CH·OH}$$
$$\text{O}$$

The author was unaware of the work of Haworth and Leitch (T., 1919, **115**, 813) on the latter subject when this paper was written. Apart from the fact that in the latter authors' formula for cellobiose both carbonyl groups are in acetal combination, the

two formulæ for cellobiose differ only in that the residues are united by an (a) combination in the case of von Euler, and a (b) combination in the case of Haworth and Leitch. A decision on this point could not be arrived at from a trimethylglucose prepared from methylated cellulose, as the fission would occur at the (b) combination in von Euler's cellulose formula in the preparation of cellobiose, but this point could be settled by the examination of the methylglucoside obtained from methylated cellobiose.

F. M. R.

Hydrolysis of Cellulose. YRJÖ KAUKO (*Naturwiss.*, 1921, 9, 237—238; from *Chem. Zentr.*, 1921, iii, 526).—By saturating moist cellulose with hydrogen chloride in the cold, a thick solution is obtained which remains almost colourless even after forty hours. The solution thus obtained reacts with Fehling's solution to the extent of 40—60% of the theoretical amount of dextrose, if complete transformation were assumed. With increasing time of reaction, increasing amounts of substances giving dextrose after autoclaving are formed. As much as 90% of dextrose may be obtained if sufficient time be allowed for the reaction. At 13°, 80% is obtained within four hours. Above this temperature, dark coloured products are obtained. The yield of dextrose is markedly increased by moistening the cellulose with larger quantities of water. A quantitative method for the estimation of cellulose might be developed, using this reaction. G. W. R.

Nature of the Swelling Process. V. Swelling and Partition in the System Nitrobenzene-Alcohol-Cellulose Acetate. E. KNOEVENAGEL and ALBERT BREGENZER (*Koll. Chem. Beihefte*, 1921, 14, 1—24; cf. this vol., i, 402, 709, 710).—The swelling of cellulose acetate in mixtures of nitrobenzene and alcohol of various compositions has been investigated at 25°. It is shown that over the range of concentrations 12—60% nitrobenzene, this substance is taken up by the cellulose acetate in such an amount that there is a constant partition relationship between the amounts in the liquid and solid phases. The alcohol is combined in a constant amount with the cellulose acetate over a long range of the lower concentrations of nitrobenzene, but at higher concentrations, 60% and upwards, the solubility of the cellulose acetate in nitrobenzene exerts a disturbing influence on this relationship. J. F. S.

Polysaccharides. IX. Cellulose and Lignin. P. KARRER and F. WIDMER (*Helv. Chim. Acta*, 1921, 4, 700—702).—Treatment of dry cellulose with acetyl bromide free from acetic acid yields a mixture of amorphous products containing bromine. Acetobromocellose and -glucose are only formed in presence of acetic acid, and in proportions which, although notable (20% of the former as a maximum by working at 40—50°), are far from quantitative, a point which differentiates cellulose from starch (cf. this vol., i, 768). The result permits of no decision as to whether cellulose is a polymeric anhydro-sugar or possesses a chain structure, since the conditions mentioned are too drastic, and at low temperatures very little

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acetobromocellose is produced. Wood, straw, and similar materials are completely dissolved by acetyl bromide. The solutions, when decomposed by ice, furnish decomposition products of cellulose and of lignin, from which the former may be removed by solution in alcohol, leaving the latter as a powder which contains bromine and does not reduce Fehling's solution. The result supports the view that lignin and cellulose are not chemically combined in wood.

J. K.

Constitution of Lignin. S. V. HINTIKKA (*Cellulosechemie*, 1921, **2**, 63—64; from *Chem. Zentr.*, 1921, iii, 619).—The contention of Klason (A., 1920, i, 474 and 821) that an acraldehyde complex, $R \cdot CH \vdots CH \vdots CHO$, occurs in lignin and that in the sulphite process a sulphonic acid, $CH_2R \cdot CH(SO_2 \cdot OH) \cdot CHO$, is first formed which gives a yellow cyclic salt with naphthylamine salts is regarded as untenable.   G. W. R.

Lignin from Straw prepared by Treatment with Alkali Carbonate. F. PASCHKE (*Zeitsch. angew. Chem.*, 1921, **34**, 465).—The lignin was prepared by treatment of the straw with an alkali carbonate, precipitation from the extract with acid, and purification by repeated solution in alkali and reprecipitation with acid. The equivalent weight, determined by solution of the purified lignin in excess of standard alkali hydroxide solution and titration with phenolphthalein and methyl-orange as indicators, with which lignin behaves similarly to carbonic acid, gave a value of 357, considerably lower therefore than the figure 462 found by Beckmann (this vol., i, 546) for lignin from winter rye straw. This high figure was partly due to colloidal lignin passing through the filter in the method he adopted. Elementary analyses of the straw lignin gave figures corresponding with either $C_2 \cdot H_{31}O_9$ or $C_{40}H_{45}O_{13}$, from which it is apparent that this lignin differs from Beckmann's essentially in its oxygen content, the formula assigned for the latter being $C_{40}H_{46}O_{15}$ (*loc. cit.*). The $C_{40}H_{45}O_{13}$ formula demands an equivalent weight of 366, assuming 1Na for each 20 C atoms. This is in close agreement with the value actually found.   G. F. M.

Unsaturated Residues in Chemical and Pharmacological Relationship. III. JULIUS VON BRAUN and OTTO BRAUNSDORF (*Ber.*, 1921, **54**, [*B*], 2081—2088).—In previous communications (A., 1918, i, 162) it has been shown that the anæsthetising action of substances containing the tropan ring is greatly increased by the introduction of a double bond. The observations have now been extended to the novocaine group, in which it is found that a similar effect is produced by the replacement of the ethyl by the allyl or cinnamyl groups, but not by the furfuryl radicle.

Ethyl-β-hydroxyethylallylamine, $C_3H_5 \cdot NEt \cdot CH_2 \cdot CH_2 \cdot OH$, a colourless liquid, b. p. 183—184°, is prepared in 40% yield by the action of molecular proportions of ethylene oxide and ethylallylamine in moist chloroform solution at 60°. It is converted by *p*-nitrobenzoyl chloride in warm benzene solution into β-*p-nitrobenzoyloxyethylethylallylamine*, $C_3H_5 \cdot NEt \cdot CH_2 \cdot CH_2 \cdot O \cdot CO \cdot C_6H_4 \cdot NO_2$, a yellow liquid

which solidifies when strongly cooled (the oily *hydrochloride*, the *platinichloride*, orange-yellow needles, m. p. 155—156°, and *picrate*, yellow platelets, m. p. 107—108°, are described). The nitro-compound is reduced by stannous chloride and hydrochloric acid to β-*p-aminobenzoyloxyethylethylallylamine*, a viscous, yellow liquid [*platinichloride*, m. p. 205° (decomp.) after darkening at 195°; *picrate*, m. p. 137°; the *hydrochloride* is extremely hygroscopic].

Ethylamine reacts with cinnamyl bromide to give *dicinnamylethyl-amine*, m. p. 44—45°, b. p. 235—240°/9 mm. (the *picrate* has m. p. 125—126°, the *hydrochloride* is oily) and *cinnamylethylamine*, a colour-less, mobile liquid, b. p. 129—131°/9 mm. (the *hydrochloride*, m. p. 163°, *platinichloride*, decomp. 206°, *picrolonate*, long prisms, m. p. 215—216°, and *picrate*, dark yellow leaflets, m. p. 120°, are described). The secondary base is transformed by ethylene oxide into *cinnamyl-ethyl-β-hydroxyethylamine*, $CHPh:CH\cdot CH_2\cdot NEt\cdot CH_2\cdot CH_2\cdot OH$, a col-ourless, moderately viscous liquid which is partly decomposed when distilled. The p-*nitrobenzoyl* compound of the latter is a viscous, yellow liquid which is best characterised by its *picrolonate*; it is reduced by stannous chloride and hydrochloric acid to *cinnamyl-β-p-aminobenzoyloxyethylethylamine*, a yellow liquid which does not give crystalline salts. The corresponding *acetyl* derivative and its *hydrochloride* and *picrate* are non-crystalline.

Furfurylethylamine, $C_4H_3O\cdot CH_2\cdot NHEt$, b. p. 168—170°, is con-verted by ethylene oxide into the corresponding β-*hydroxyethyl* derivative, a pale yellow liquid, b. p. 127°/12 mm. (the *picrate* and *picrolonate*, m. p. 159°, are described). The p-*nitrobenzoyl* compound of the latter is oily, but yields crystalline salts of which the *picrolonate*, m. p. 164°, and *picrate*, m. p. 119°, have been examined. β-p-*Aminobenzoyloxyethylfurfurylethylamine* is also a liquid; it yields an indistinctly crystalline *picrate*.   H. W.

Behaviour of certain Acyl Derivatives of Allylamine to-wards Halogens.

MAX BERGMANN, FERDINAND DREYER, and FRITZ RADT (*Ber.*, 1921, **54**, [B], 2139—2150).—The bromination of allylacetamide has been examined by Chiari (A., 1899, i, 325), who, in spite of the abnormal course of his experiments, considered the process to occur in the orthodox manner with the formation of the dibromo-derivative. This is now shown to be the case in part, but during the reaction a wandering of the acetyl group is also observed so that the change may be represented by the scheme :

$$NHAc\cdot CH_2\cdot CHBr\cdot CH_2Br \xleftarrow{\text{addition}} NHAc\cdot CH_2\cdot CH:CH_2 \xrightarrow[+H_2O]{\text{transformation}}$$

$CH_2Br\cdot CH(OAc)\cdot CH_2\cdot NH_2,HBr$. A similar transformation is ob-served with the corresponding benzoyl and, to a less extent, with the bromoacetyl derivative, but not with the urethane. It is a matter of indifference whether bromination is effected with dry or moist substances. The dibromides are converted into the hydro-bromides when heated alone or in the presence of water, so that it appears that they themselves or their precursors play a decisive part in the formation of the hydrobromides during the bromina-tion of acylallylamines. This view is maintained, although it is

shown that the pre-formed dibromides are perfectly stable under
the experimental conditions of the bromination and is justified by
a series of examples taken from the literature by which it is shown
that the stability of a compound in a state of rest cannot be taken
as a criterion of its stability when formed under certain conditions
of reaction.

Benzoallylamide is converted by bromine in moist chloroform
solution into a mixture of benzo-N-βγ-dibromo-*n*-propylamide,
m. p. 135°, and *γ-bromo-α-aminoisopropyl benzoate hydrobromide,*
$CH_2Br\cdot CH(OBz)\cdot CH_2\cdot NH_2, HBr$, colourless, microscopic needles,
m. p. 188—189° (decomp.) after previous softening when rapidly
heated. If the salt is treated with sufficient alkali to neutralise
the hydrobromic acid, the liberated base rapidly becomes isomerised
to *benzo-γ-bromo-β-hydroxypropylamide,* thin, hexagonal plates,
m. p. 115°, the p-*nitrobenzoate* of which forms microscopic needles,
m. p. 146°. Similarly, the chlorination of benzoallylamide yields
benzo-βγ-dichloropropylamide and relatively larger amounts of α-
chloro-β-benzoxypropylamine hydrochloride which was analysed in
the form of its *picrate*, m. p. 181°.

The bromination of acetoallylamide leads to the formation of
aceto-βγ-dibromo-*n*-propylamide, m. p. 65° (indefinite), and γ-
bromo-β-acetoxypropylamine hydrobromide, long needles, m. p. 159—
161° (*picrate*, short, rhombic prisms, m. p. 124—126°); the latter
substance is also formed by the transformation of the dibromide
in the presence of water at 100°.

N-Allylurethane is transformed by bromine into N-βγ-*dibromo-*
n-propylurethane, $CH_2Br\cdot CHBr\cdot CH_2\cdot NH\cdot CO_2Et$, short needles, m. p.
44°.

Bromination of *bromoacetoallylamide,* b. p. 85°/0·3—0·4 mm.,
leads to the production of *bromoaceto-βγ-dibromo-n-propylamide,*

$$CH_2Br\cdot CHBr\cdot CH_2\cdot NH\cdot CO\cdot CH_2Br,$$
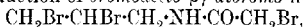
needles or prisms, m. p. 77—79°, and *α-bromo-β-bromoacetoxypropyl-*
amine hydrobromide, $CH_2Br\cdot CH(O\cdot CO\cdot CH_2Br)\cdot CH_2\cdot NH_2, HBr$, irreg-
ular quadratic plates, m. p. 150°; the latter substance is also
obtained when the dibromide is boiled with water. The corre-
sponding *picrate* crystallises in small, yellow prisms, m. p. 154—
156°. The hydrobromide is transformed by the equivalent quantity
of *N*-sodium hydroxide solution into *bromoaceto-γ-bromo-β-hydroxy-*
propylamide, $CH_2Br\cdot CH(OH)\cdot CH_2\cdot NH\cdot CO\cdot CH_2Br$, thin, rhombic
plates, m. p. 86—87°.   H. W.

Preparation of Additive Products of Hexamethylenetetr-
amine. J. D. RIEDEL, AKT. GES. (D.R.-P. 338427; from *Chem.*
Zentr., 1921, iv, 588—589).—The additive products obtained from
monohalogen acetic acids and hexamethylenetetramine (D.R.-P.
334709) are rather unstable in solution. Their metallic salts,
which are more stable, are prepared by usual methods.   G. W. R.

Preparation of Derivatives of Hexamethylenetetramine.
J. D. RIEDEL AKT. GES., and FR. BOEDECKER (D.R.-P.
338428; from *Chem. Zentr.*, 1921, iv, 589; cf. preceding abstract).
—Hexamethylenetetramine is allowed to react with metallic

salts of monohalogen acetic acids whereby quaternary salts are formed.　　　　　　　　　　　　　　　　　　　　　　　G. W. R.

Synthesis of Formamide from Carbon Monoxide and Ammonia. KURT H. MEYER and LUDWIG ORTHNER (*Ber.*, 1921, **54**, [*B*], 1705—1709).—Formamide is obtained in small amount by heating carbon monoxide and ammonia in a steel tube in the presence of porous clay at 200° under a final pressure of 170 atmospheres. Ammonium carbonate, formate, and cyanide are produced simultaneously. Below 180°, the rate of reaction is too small, whilst above 200° the yields are too low; formamide is almost completely decomposed at 227°.　　　　　　　H. W.

Bromural [α-Bromo*iso*valerylcarbamide]. E. YOSHITOMI and K. WATANABE (*J. Pharm. Soc. Japan*, 1921, No. **468**, 125—130).—In the preparation of α-bromo*iso*valerylcarbamide by way of *iso*amyl alcohol, *iso*valeric acid, and α-bromo*iso*valeryl bromide, condensation products of carbamide with α-methylbutyric acid and *iso*valeric acid are also formed. The commercial product has m. p. 145—156°, whereas the pure substance has m. p. 154°. It is shown, however, that m. p. determinations will not indicate the purity of bromural when *iso*valerylcarbamide is present as an impurity.　　　　　　　　　　　　CHEMICAL ABSTRACTS.

α-Bromohexoylcarbamide and Homologous Straight Chain Bromoacyl Derivatives of Carbamide. M. TIFFENEAU and ET. ARDELY (*Bull. Sci. Pharmacol.*, 1921, **28**, 155—160; from *Chem. Zentr.*, 1921, iii, 366).—In a study of the bromoacyl derivatives of carbamide the following compounds were prepared : α-*Bromohexoylcarbamide*, $CH_2Me \cdot [CH_2]_2 \cdot CHBr \cdot CO \cdot NH \cdot CO \cdot NH_2$, prepared from bromohexoyl chloride and carbamide; it crystallises in fine needles, m. p. 134°; α-hydroxyhexoylcarbamide is formed on boiling with water. α-*Bromoheptoylcarbamide* has m. p. 136°. α-*Bromononoylcarbamide* crystallises in silky needles, m. p. 176°. α-*Bromolaurylcarbamide* forms fibrous masses, m. p. 186°. Straight-chain derivatives have a simple diuretic action without any hypnotic effect. The physiological effect of other derivatives is to be attributed to branched chains rather than to the presence of halogen.　　　　　　　　　　　　　　　　　G. W. R.

Ethyl- and Allyl-selenocarbamides and their Alkyl Haloids. HANS SCHMIDT (*Ber.*, 1921, **54**, [*B*], 2067—2070).—*Ethylselenocarbamide*, $NHEt \cdot CSe \cdot NH_2$, colourless needles, m. p. 125°, is prepared by treating a solution of ethylcyanamide in anhydrous ether with hydrogen selenide at the atmospheric temperature in the absence of air and in subdued light. The substance rapidly becomes red owing to the separation of selenium when exposed to light, but can be preserved indefinitely in sealed vessels in the dark. The selenium atom is far more labile than the sulphur atom in the corresponding thio-compound. The substance unites with allyl bromide in alcoholic solution at 60—70°, giving the additive *product*, $NHEt \cdot C(NH_2) \colon SeBr \cdot C_3H_5$, or $NHEt \cdot C(\colon NH) \cdot Se \cdot C_3H_5, HBr$, m. p. 115°. *Allylselenocarbamide* forms colourless crystals, m. p.

about 93°, and has an intensely irritant effect on the skin; with ethyl iodide, it yields a colourless, additive *compound*, $C_6H_{13}N_2ISe$, m. p. 100°.   H. W.
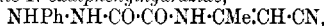
The Constitution of Hydrocyanic Acid. KURT H. MEYER and HEINRICH HOPFF (*Ber.*, 1921, **54**, [*B*], 1709—1714).—Adopting a method similar to that used with ethyl acetoacetate (A., 1920, i, 717), the authors have endeavoured to separate anhydrous hydro-cyanic acid into two different fractions, but without success, since the separate portions are found to have a constant refractive index ($n_D^{16°}$ 1·2715). Hydrocyanic acid cannot therefore be a mixture of two isomerides with a finite velocity of transformation and, since the molecular refraction of the liquid is identical with that of the gaseous acid, it is very improbable that it can be a mixture with high velocity of interconversion. The possibility of the presence of a small amount of the *iso*-form, as exhibited by ethyl malonate and methanetricarboxylate (A., 1912, i, 941), is not, however, excluded. Attempts to deduce the constitution of the acid from physical data are recorded; the substance has $d_4^{19°}$ 0·7018 ($\pm 0·0002$), n_D 1·2675, n_α 1·2661, n_β 1·2713, n_γ 1·2752, $n_\gamma - n_\alpha$ 0·0091, and com-parison of these values with those calculated for the nitrile and *iso*nitrile forms indicates that free hydrocyanic acid is identical with formonitrile. Considerations of thermochemical data (cf. Lemoult, A., 1907, ii, 10) indicate that, at the atmospheric temperature, hydrocyanic acid is formonitrile containing minute amounts of carbylamine and that the proportion of the latter increases some-what with increasing temperature.   H. W.
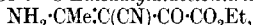
Oxalic Acid Derivatives of "Diacetonitrile." ERICH BENARY and MAX SCHMIDT (*Ber.*, 1921, **54**, [*B*], 2157—2168.)—Diacetonitrile is shown to behave towards ethoxalyl chloride and ethyl oxalate in the same manner as ethyl β-aminocrotonate (A., 1917, i, 252).

N-Ethoxalyldiacetonitrile (cf. Fleischhauer, A., 1893, i, 396), m. p. 93°, is proved definitely to be a N-derivative by its conversion into *diacetonitrile*-N-*oxalphenylhydrazide*,
$$NHPh \cdot NH \cdot CO \cdot CO \cdot NH \cdot CMe:CH \cdot CN,$$
yellow needles, m. p. 192° (decomp.), which is decomposed by boiling dilute sulphuric acid with formation of oxalamidephenyl-hydrazide, m. p. 235°. C-*Ethoxalyldiacetonitrile*,
$$NH_2 \cdot CMe:C(CN) \cdot CO \cdot CO_2Et,$$
long, colourless needles, m p. 114—115°, is obtained by the inter-action of diacetonitrile, pyridine, and ethoxalyl chloride in absolute ethereal solution; the corresponding *amide*, colourless, pointed needles which carbonise above 195°, and *anilide*, lustrous, yellow leaflets, decomp. 203—207°, are described. The ester is slowly transformed by concentrated hydrochloric acid at the atmospheric temperature into *diacetonitrile*-C-*oxaliminolactone*,
$$\begin{array}{c} NH:CMe \cdot CH \cdot C(NH) \\ CO \underline{\quad\quad} CO \end{array} \!\!> O,$$
colourless, hexagonal pyramids, incipient decomp. 230°; the same substance is obtained when the ester is treated with the calculated
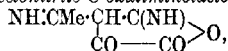
quantity of sodium hydroxide, barium hydroxide, or sodium carbonate solution, but a portion of it is also decomposed into oxalic acid and ammonia. It is converted by aniline in boiling dilute acetic acid solution into the corresponding *anilino*-derivative, NPh:CMe·CH·C(NH)
$\underset{\text{CO}\text{---}\text{CO}}{\Big\rangle}$O, golden-yellow, lustrous leaflets, m. p.
236°. Diacetonitrile-C-oxamide is slowly transformed by boiling water into *ammonium diacetonitrile-C-oxalate*, colourless four-sided prisms (+H$_2$O), decomp. 180—220° (the corresponding *silver* and *copper* salts are described); *diacet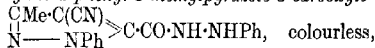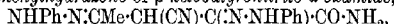onitrile-C-oxalic acid*, NH:CMe·CH(CN)·CO·CO$_2$H, is isolated from the copper salt in the form of small, yellow crystals which are too hygroscopic to permit analysis or determination of the melting point.
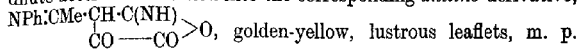
C-Ethoxalyldiacetonitrile and phenylhydrazine in 50% acetic acid solution give *4-cyano-1-phenyl-3-methylpyrazole-5-carboxylo-*
phenylhydrazide, $\underset{\text{N}\text{---}\text{NPh}}{\overset{\text{CMe·C(CN)}}{\Big\rangle}}$C·CO·NH·NHPh,   colourless,
rectangular leaflets, m. p. 207°, which is hydrolysed by sodium hydroxide solution to 4-carboxy-1-phenyl-3-methylpyrazole-5-carboxyphenylhydrazide, pointed needles, m. p. 253°, which is identical with the acid prepared previously (*loc. cit.*) by hydrolysis of the compound formed from ethyl β-aminocrotonate and phenylhydrazine. The cyano-compound is oxidised by potassium permanganate in acetone solution to 4-*cyano-1-phenyl-3-methylpyrazole-5-carboxylic acid*, colourless, four-sided prisms, m. p. 211—212° (decomp.), which passes when heated into 4-*cyano-1-phenyl-3-methylpyrazole*, prisms, m. p. 93—94°. The cyanocarboxylic acid is converted by sodium hydroxide solution into the previously described 1-phenyl-3-methylpyrazole-4 : 5-dicarboxylic acid.

The *diphenylhydrazone* of β-*ketobutyronitrile-α-oxamide*,
NHPh·N:CMe·CH(CN)·C(:N·NHPh)·CO·NH$_2$,
prepared from C-ethoxalyldiacetonitrile and phenylhydrazine in boiling alcoholic solution, forms long, pointed needles, m. p. 232°. 4-*Cyano-1-phenyl-3-methylpyrazole-5-carboxyanilide*, from *diacetonitrile-O-oxanilide* and phenylhydrazine in boiling alcoholic solution, crystallises in colourless needles, m. p. 167—168°.   H. W.

The Reducing Action of the Grignard Reagent and the Existence of Magnesium Hydrogen Haloid. KURT HESS and HEINRICH RHEINBOLDT (*Ber.*, 1921, **54**, [*B*], 2043—2055).—A series of experiments is described which has for its object the preparation of magnesium hydrogen haloids, H·Mg·Hal. It is found that, under the conditions customary in the preparation of Grignard's reagents, magnesium does not react with gaseous hydrogen chloride in the presence of ether or benzene. Liquid hydriodic acid does not attack magnesium whereas in the presence of dry ether a reaction occurs readily which, however, is due to the ready conversion of ether into ethyl iodide by hydrogen iodide. To avoid complications of this type, the "individual" Grignard compounds were used, when it was found that magnesium ethyl iodide does not react with gaseous or liquid hydrogen iodide, alone

or in the presence of benzene, whereas it is decomposed completely by hydrogen chloride with the liberation of ethane. Attempts to demonstrate the unaltered nature of the magnesium ethyl iodide after treatment with hydrogen iodide by bringing it into reaction with benzaldehyde led to the rather surprising isolation of benzyl alcohol instead of the expected phenylethylcarbinol. A similar result was observed with untreated magnesium ethyl iodide in warm benzene and, but to a less extent, in warm ether, whereas phenyl-ethylcarbinol was exclusively obtained in ethereal solution at the atmospheric temperature.

Individual cases of reduction by Grignard's reagent have been recorded previously, but have not received any general explanation. According to the authors, they can be represented most accurately by the co-ordination formulæ, $RR'C:O\cdots Mg<^{Br}_{CH_2 \cdot CH_3}$, and the reactions then occur in accordance with the scheme:

$$Mg<^{X}_{OH} + ^{R}_{R'}>C<^{OH}_{CH_2 \cdot CH_3} \xrightarrow[+H_2O]{\text{in the cold}} ^{R}_{R'}>C:O\cdots Mg<^{X}_{CH_2 \cdot CH_3}$$

$$\xrightarrow{\text{warmed}} ^{R}_{R'}>C:O\cdots Mg<^{X}_{H} + ^{CH_2}_{CH_2} \xrightarrow{+H_2O} ^{R}_{R'}>C<^{OH}_{H} + Mg<^{X}_{OH}$$
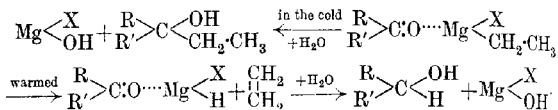
Since it is shown that the subsidiary reaction may be made into the main change by increasing the temperature, it is possible that a method is opened out for the reduction of substances containing a ketonic group and other reducible groups (for example, ethylenic linkings) which are not changed by reduction of the ketonic group. In any case, it is demonstrated that the avoidance of subsidiary reactions in the case of the aliphatic alkyl haloids (except the methyl compounds) can only be secured by the avoidance of elevated temperature, except under perfectly definite conditions.   H. W.

The Benzene [Formula] Problem. V. The Benzene Ring in Substitution Products.

A. VON WEINBERG (*Ber.*, 1921, 54, [*B*], 2171—2175).—The introduction of a substituent into the benzene ring causes an alteration in the aromatic character the extent of which depends on the nature, number, and position of the substituents. It is shown by a series of examples that the abnormal deviations can be considered mathematically in the cases of the molecular refraction, absorption spectra, and energy content. Increase in volume (as indicated by molecular refraction) is accompanied by increase in the wave-length of the absorption band of maximal intensity and by a parallel decrease of the energy content.   H. W.

Nitrogen Dioxide. I. Nitration with Nitrogen Dioxide.

HEINRICH WIELAND [with C. REISENEGGER] (*Ber.*, 1921, 54, [*B*], 1776—1784; cf. Wieland and Blümich, this vol., i, 552).—The behaviour of nitrogen dioxide towards aromatic compounds has been investigated.

Pure nitrogen dioxide does not react with cold aromatic hydrocarbons; with benzene at 80°, the main products are 1 : 3 : 5-trinitrobenzene and picric acid, together with smaller amounts of unchanged benzene, nitrobenzene, carbon dioxide, oxalic acid, and nitrogenous substances which are soluble in water and belong to the fatty series. The production of the trinitro-derivatives in the presence of unchanged benzene indicates that the process is one of primary addition to a hexanitro-derivative followed by elimination of nitrous acid and not of step-wise nitration; this is confirmed further by the observation that nitrobenzene is indifferent towards nitrogen dioxide at 80°.

[With A. BERNHEIM and P. BÖHM.]—Phenol is readily nitrated when dissolved in a cold mixture of benzene and light petroleum and treated with a solution of nitrogen dioxide in the same solvents; a mixture of o- and p-nitrophenols is obtained, the total weight of which is 125% of that of the phenol used. Tarry by-products are not observed. o-Cresol yields o- and p-nitro-o-cresol, m-cresol gives o- and p-nitro-m-cresol, whilst the p-compound yields o-nitro-p-cresol and o-dinitro-p-cresol. m-4-Xylenol is converted into the corresponding 5-nitro-compound. α-Naphthol gives a mixture of 2-nitro-α-naphthol and 2 : 4-dinitro-α-naphthol. Reaction does not occur with anisole.

Acetanilide does not suffer nitration in the nucleus; the acetyl group is removed and benzenediazonium nitrate results.

The action of nitrogen dioxide on diphenylamine depends greatly on the solvent used; with ether, it is converted into diphenylnitrosoamine, whereas in the presence of benzene it gives p-nitrodiphenylnitrosoamine. In the former case the reaction is explained by the observation that absolute ether reacts readily with nitrogen dioxide with the formation of ethyl nitrite, $Et_2O+N_2O_4 \rightarrow EtO\cdot NO + EtO\cdot NO_2$; in the latter instance, the primary action doubtless consists of nitration in the nucleus, the nitroso-group being introduced subsequently by the liberated nitrous acid.

The constitution of nitrogen trioxide and peroxide is discussed; the conception of the latter as a mixed anhydride of nitrous and nitric acids, $O:N\cdot O\cdot NO_2$, is in harmony with its action towards alkali, but the similar conception of nitrogen trioxide as $O:N\cdot O\cdot N:O$ is not in keeping with its intense blue colour in accordance with which it must be regarded as a nitroso-derivative, $O:N\cdot NO_2$. The corresponding formula, $O_2N\cdot NO_2$, is also very probable for the peroxide by reason of its reactions and dissociability; its decomposition by alkali is then analogous to that of other symmetrically-paired atoms or radicles, for example, cyanogen to cyanide and cyanate, chlorine to chloride and hypochlorite.　　　H. W.

Transformation or (and) Hydrolysis of the Toluene-p-sulphonyl Compounds of certain para-Substituted Anilines and their N-Alkyl Derivatives. J. HALBERKANN (*Ber.*, 1921, **54**, [*B*], 1833—1849).—In a previous communication (this vol., i, 661) it has been shown that p-toluenesulphonyl-p-anisidide is convertible by sulphuric acid into 2-amino-5-methoxyphenyl-p-

tolylsulphone and thus forms an exception to Witt's rule (A., 1913, i, 360; 1914, i, 228), according to which the sulphon-amides of primary bases only suffer hydrolysis, whilst those of secondary bases suffer transformation. A more extended study has confirmed the general validity of the rule in so far as the primary bases are concerned, and has shown that the behaviour of the p-anisidide is exceptional. In its present form, however, the statement of the rule is too general in the case of the sulphonamides of secondary bases; many of these readily undergo hydrolysis with the production of pure secondary bases and all of them can be caused to do so by the use of suitably dilute sulphuric acid, thus giving the simplest method available at present for the preparation of pure secondary amines.

Toluene-p-sulphonyl-p-toluidide is converted by sulphuric acid (d 1·84) at 130° into p-toluidine-o-sulphonic acid and by rapid treatment at 55° into small amounts of o-aminodi-pp'-tolylsulphone, m. p. 166°; with the acid (d 1·74) at 130°, p-toluidine (88%), together with traces of the sulphone and toluidinesulphonic acid, is produced, whilst the 70% acid causes quantitative hydro-lysis to p-toluidine. N-p-*Toluenesulphonylmethyl*-p-*toluidide*, $C_6H_4Me\cdot NMe\cdot SO_2\cdot C_6H_4Me$, large, colourless rods, m. p. 60° (from the preceding compound and methyl sulphate in alkaline solution), is almost quantitatively converted by the action of sulphuric acid (d 1·84) at 100° into 6-*methylamino*-m-*tolyl*-p-*tolylsulphone*, $C_6H_4Me\cdot SO_2\cdot C_6H_3Me\cdot NHMe$, colourless, fluorescent, prismatic plates, m. p. 138° (corresponding *acetyl* derivative, colourless, prismatic needles, m. p. 149—150°); with sulphuric acid (d 1·74) at 120°, N-methyl-p-toluidine is mainly produced together with small amounts of the sulphone, whilst the acid (d 1·67) causes quanti-tative hydrolysis. N-p-Toluenesulphonylethyl-p-toluidide, coarse, colourless prisms, m. p. 51—52° (Witt, *loc. cit.*, gives m. p. 71—72°), behaves similarly to the methyl compound. *Toluene*-p-*sulphonyl*-p-*nitroanilide*, yellow prisms, m. p. 191° (from the com-ponents in the presence of pyridine), is hydrolysed by sulphuric acid (d 1·84, 1·74, or 1·6). N-p-Toluenesulphonylmethyl-p-nitro-anilide, yellow prisms, m. p. 176° (Morgan and Micklethwait, T., 1912, **101**, 146, give m. p. 182°), could not be isomerised to the sulphone, but is smoothly converted into N-methyl-p-nitroaniline. Similarly, isomerisation could not be induced in the cases of toluene-p-sulphonyl-p-aminoanilide, or N-p-toluenesulphonylmethyl-p-aminoanilide, from which the corresponding bases are produced quantitatively. Toluene-p-sulphonyl-p-sulphonanilide,

$$C_6H_4Me\cdot SO_2\cdot NH\cdot C_6H_4\cdot SO_3H,$$
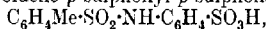
is obtained in the form of its *pyridine* salt, long, colourless, pris-matic needles (+1H₂O), m. p. 177°; it is quantitatively hydrolysed to sulphanilic acid by sulphuric acid (d 1·84) at 95° or (d 1·74) at 110°. *Sodium* p-*toluenesulphonylmethylsulphanilate*, $C_6H_4Me\cdot SO_2\cdot NMe\cdot C_6H_4\cdot SO_3Na$, colourless, slender needles (+2H₂O), decomp. about 295°, is hydrolysed by sulphuric acid (d 1·84 or 1·74) to N-*methyl*-p-*sulphanilic acid*, colourless, lustrous plates, m. p.

244—245° (decomp.). Toluene-*p*-sulphonyl-*p*-chloroanilide, m. p. 95—96° (*acetyl* compound, long, prismatic needles, m. p. 154°), could not be isomerised. p-*Toluenesulphonylmethyl*-*p*-*chloroanilide*, colourless crystals, m. p. 96—97°, is almost quantitatively hydrolysed by sulphuric acid to N-methyl-*p*-chloroaniline, b. p. 242°/768 mm.; small amounts (6%) of 5-*chloro*-2-*methylaminophenyl*-*p*-*tolylsulphone*, $C_6H_4Me\cdot SO_2\cdot C_6H_3Cl\cdot NHMe$, colourless prisms, m. p. 156° (*acetyl* derivative, m. p. 157—158°), are produced simultaneously.　　　　　　　　　　　　　　　　H. W.

The Benzene [Formula] Problem. IV. The Naphthalene Formula. A. VON WEINBERG (*Ber.*, 1921, **54**, [*B*], 2168—2171).— The theory of intramolecular vibration has led the author previously (A., 1919, i, 314) to assign a symmetrical formula to naphthalene. The unsymmetrical formulæ of von Auwers and Frühling (this vol., ii, 230) and of Mayer and Bansa (this vol., i, 175) are criticised. The following is propounded as a safe empirical rule for the recognition of aromatic nuclei : " Only aromatic amino-derivatives yield diazo-compounds which can be coupled to azo-dyes and only in the case of aromatic substances is it possible to introduce a hydroxyl group by sulphonation and subsequent fusion with alkali." From both points of view, the symmetrical, purely aromatic structure of benzene appears to be one of the most firmly established facts of organic chemistry.

The author's formula for naphthalene involves the assumption that the β-carbon atoms are in more intense vibration than the α-carbon atoms; evidence in favour of this view is found in von Auwers and Frühling's measurements of a number of α- and β-derivatives of naphthalene.　　　　　　　　　　　H. W.

The Fluorene Series. V. 2 : 7-Dichlorofluorene. A. SIEGLITZ and J. SCHATZKES (*Ber.*, 1921, **54**, [*B*], 2072—2078).—It has been shown previously (A., 1920, i, 605) that the methylene group of 2 : 7-dibromofluorene is considerably more reactive than that of the parent hydrocarbon; this is now shown to be also true of 2 : 7-dichlorofluorene.

2 : 7-Dichlorofluorene, flat plates or needles, m. p. 128°, is prepared according to the directions of Hodgkinson and Matthews (T., 1883, **43**, 170) and the position of the halogen atoms is proved definitely by conversion of the substance into 2 : 7-dichlorofluorenone. It condenses with the requisite aldehyde in boiling alcoholic solution in the presence of sodium ethoxide to yield the following derivatives (2 : 2′ : 7 : 7′-*tetrachloro*-αδ-*dibiphenylene*-Δ^αγ-*butadiene*, small, cinnabar-red needles which do not melt below 300°, is invariably formed as by-product) : 2 : 7-*dichloro*-9-*benzylidene*-*fluorene*, pale yellow rods, m. p. 94°; 2 : 7-*dichloro*-9-*o*-*methyl*-*benzylidenefluorene*, yellow rods, m. p. 142—143°; 2 : 7-*dichloro*-9-m-*methylbenzylidenefluorene*, pale yellow crystals, m. p. 96—97°; 2 : 7-*dichloro*-9-p-*methylbenzylidenefluorene*, long, lemon-yellow needles, m. p. 148°; 2 : 7-*dichloro*-9-p-iso*propylbenzylidenefluorene*,

pale yellow rods, m. p. 94—95°; 2 : 2′ : 7 : 7′-*tetrachloroisophthalyl-idenedi*-9 : 9′-*fluorene*, bright yellow needles, m. p. 253—254°; 2 : 7-*dichloro*-9-*p-aldehydobenzylidenefluorene*, deep yellow needles, m. p. 204—205°; 2 : 2′ : 7 : 7′-*tetrachloro*-9 : 9′-*diterephthalylidene-difluorene*, egg-yellow needles which do not melt below 285°; 2 : 7-*dichloro*-9-*o-chlorobenzylidenefluorene*, slender, pale orange-yellow needles, m. p. 159—160°; 2 : 7-*dichloro*-9-*m-chlorobenzyl-idenefluorene*, yellow needles, m. p. 134—135°; 2 : 7-*dichloro*-9-*p-chlorobenzylidenefluorene*, matted, lemon-yellow needles, m. p. 204—205°; 2 : 7-*dichloro*-9-2′ : 6′-*dichlorobenzylidenefluorene*, canary yellow leaflets, m. p. 212—213°; 2 : 7-*dichloro*-9-*m-bromobenzylidene-fluorene*, microscopic, yellow needles, m. p. 146—147°; 2 : 7-*dichloro*-9-*p-anisylidenefluorene*, long, dark yellow needles, m. p. 126—127°; 2 : 7-*dichloro*-9-*piperonylidenefluorene*, orange-yellow needles, m. p. 165°; 2 : 7-*dichloro*-9-*o-nitrobenzylidenefluorene*, microscopic, yellow needles, m. p. 173—174°; 2 : 7-*dichloro*-9-*m-nitrobenzylidenefluorene*, lemon-yellow needles, m. p. 180—181°; 2 : 7-*dichloro*-9-*p-nitro-benzylidenefluorene*, yellow needles, m. p. 196—197°; 2 : 7-*dichloro*-9-*cinnamylidenefluorene*, dark orange needles, m. p. 191°; 2 : 7-*dichloro*-9-*furfurylidenefluorene*, greenish-yellow needles, m. p. 190—191°; *ethyl* 2 : 7-*dichloro*-9-*fluoreneglyoxylate*, lustrous, yellow needles, m. p. 155—156° (*benzoyl* derivative, m. p. 156—157°).

The following fulvanes of 2 : 7-dichlorofluorene are prepared by reduction of the corresponding fulvene with aluminium amalgam in moist ethereal solution : 2 : 7-*dichloro*-9-*benzylfluorene*, colourless leaflets, m. p. 110—111°; 2 : 7-*dichloro*-9-*methylbenzylfluorene*, colourless leaflets, m. p. 136—137°; 2 : 7-*dichloro*-9-*p-isopropyl-benzylfluorene*, colourless needles, m. p. 115°; 2 : 7-*dichloro*-9-*o-chlorobenzylfluorene*, colourless leaflets, m. p. 116—117°; 2 : 7-*dichloro*-9-2′ : 6′-*dichlorobenzylfluorene*, long, colourless needles, m. p. 129—130°; 2 : 7-*dichloro*-9-*p-anisylfluorene*, colourless leaflets, m. p. 137—138°.

2-*Nitro*-9-*p-chlorobenzylidenefluorene* crystallises in dull yellow, microscopic needles, m. p. 246°.   H. W.

Nitration. HEINRICH WIELAND and FRANZ RAHN (*Ber.*, 1921, **54**, [B], 1770—1775).—It has been shown previously (Wieland and Sakellarios, A., 1920, i, 280) that ethylene is converted by nitrating acid into a mixture of ethylene dinitrate and β-nitroethyl nitrate, and hence that the primary process of nitration is the same in the aliphatic as in the aromatic series. In this instance, however, simultaneous esterification which is guaranteed by the presence of sulphuric acid is necessary for the protection of the product against further oxidation. In the present communication, a number of instances is recorded in which nitric acid is added directly at an aliphatic double bond; the most remarkable feature is the striking readiness with which such addition occurs.

αα-Diphenylethylene is converted by absolute nitric acid in carbon tetrachloride solution at −10° into β-nitro-αα-diphenyl-ethyl alcohol, OH·CPh₂·CH₂·NO₂, colourless crystals, m. p. 106°, which is identical with the substance described by Anschütz and

Romig (A., 1886, 1033) as " diphenylglycol mononitrite " (cf. also Anschütz and Hilbert, following abstract). In a similar manner, phenanthrene gives the ether (annexed formula), colourless, slender needles, m. p. 167° (cf. Schmidt, A., 1901, i, 76). The primary product of the action of nitric acid on β-methyl-Δβ-butylene could not be isolated, the reaction leading to the production of γ-nitro-β-methyl-Δβ-butylene, CMe₂:CMe·NO₂, an almost colourless liquid, b. p. 79—80°/17 mm., and *nitroisoamyl nitrate*, b. p. 135°/17 mm.

[With F. REINDEL.]—A solution of αα-diphenylethylene in light petroleum is transformed by nitrogen peroxide into αβ-*dinitro-αα-diphenylethane*, colourless needles, m. p. 68°, which is converted by sodium hydroxide solution into β-nitro-αα-diphenylethylene, m. p. 87° (cf. Anschütz and Romig, *loc. cit.*). The remarkable rapidity with which nitric acid is added at the double bond is illustrated by the observation that β-nitro-αα-diphenylethyl alcohol is the sole product of the action of nitrogen peroxide on αα-diphenyl-ethylene if extreme care in excluding the presence of every trace of moisture is not taken.   H. W.

Action of Nitric Acid on αα-Diphenylethane and αα-Diphenyl-ethylene. RICHARD ANSCHÜTZ and ALFRED HILBERT (*Ber.*, 1921, 54, [B], 1854—1859).—In connexion with the recent publication of Wieland and Sakellarios (A., 1920, i, 280; cf. Wieland and Rahn, preceding abstract), the authors have repeated the work of Anschütz and Romig (A., 1886, 1033) on the nitration of αα-diphenyl-ethane and αα-diphenylethylene in glacial acetic acid solution. The products described previously as diphenylethylene glycol mononitrite, diphenylvinyl nitrite, and " dinitrite " are shown to be β-nitro-αα-diphenylethyl alcohol, β-nitro-αα-diphenylethylene, and ββ-dinitro-αα-diphenylethylene respectively, the course of the change being indicated by the scheme : CPh₂:CH₂ $\xrightarrow{+HNO_3}$ OH·CPh₂·CH₂·NO₂ $\xrightarrow{-H_2O}$ CPh₂:CH·NO₂ $\xrightarrow{+HNO_3}$ OH·CPh₂·CH(NO₂)₂ $\xrightarrow{-H_2O}$ CPh₂:C(NO₂)₂. The reduction of the latter to diphenyl-acetonitrile occurs in the following manner : CPh₂:C(NO₂)₂ $\xrightarrow{12H}$ CPh₂:C(NH₂)₂ $\xrightarrow{-NH_3}$ CPh₂:C:NH $\longrightarrow$ CHPh₂·CN. The same substances are also produced from diphenylethane; this is due to oxidation of the latter to diphenylmethylcarbinol, which is converted with loss of water into diphenylethylene.

The authors give a facsimile of a private communication of Kekulé which shows that the latter, in 1877, considered the product of the action of nitric acid on ethylene to be nitroethyl nitrate.
                                         H. W.

Reduction of Organic Halogen Compounds. IV. The Tetra-arylbutane Series and ααδδ-Tetraphenylbutatriene. K. BRAND (*Ber.*, 1921, 54, [B], 1987—2006; cf. A., 1913, i, 1169, 1170).—Temporary inability to obtain the requisite supply of

electricity has led the author to continue his experiments with chemical reducing agents.

βββ-Trichloro-αα-diphenylethane is reduced by Devarda's or Arndt's alloy in boiling alcoholic (95%) solution to *ββγγ-tetrachloro-ααδδ-tetraphenylbutane*, $CHPh_2 \cdot CCl_2 \cdot CCl_2 \cdot CHPh_2$, colourless needles, m. p. 188—190°; acetaldehyde and tetraphenyldichlorobutene are also produced, whilst much βββ-trichloro-αα-diphenylethane remains unattacked. In general, the yields are not particularly good, and the method is less suitable than the electrochemical process. When treated similarly, βββ-tribromo-αα-diphenylethane gives a mixture of *βββγγ-tetrabromo-ααδδ-tetraphenylbutane*, colourless crystals, m. p. 196—197°, and probably of the stereoisomeric *βγ-dibromo-ααδδ-tetraphenyl-Δ^β-butenes*, colourless needles, m. p. about 130—131°. ββγγ-Tetrachloro-ααδδ-tetraphenylbutane is reduced by zinc dust in boiling glacial acetic acid solution to βγ-dichloro-ααδδ-tetraphenyl-Δ^β-butene, which is separable by fractional crystallisation from light petroleum and alcohol into the stereoisomeric *forms*, m. p. 106—108° and 137—138°, respectively; the fractions appear to be uniform under the microscope, but the melting points are not very definite. A similar elimination of two atoms of halogen occurs when the tetrachloro-compound is treated with zinc dust and alcohol or with hydrogen in the presence of palladianised calcium carbonate, or is reduced electrochemically at a lead cathode; in no case is the halogen replaced by hydrogen. ββγγ-Tetrabromo-ααδδ-tetraphenylbutane, on the other hand, loses the whole of its bromine when subjected to reduction, and is converted, for example, by zinc dust in boiling glacial acetic acid solution, into ααδδ-tetraphenyl-Δ^β-butinene, $CHPh_2 \cdot C \vdots C \cdot CHPh_2$, colourless needles, m. p. 116°. βγ-Dichloro-ααδδ-tetraphenyl-Δ^β-butene is remarkably stable towards bromine, chlorine, potassium permanganate, and chromic acid in glacial acetic acid solution, with the latter of which it yields benzophenone in very small amount. It is transformed by boiling alcoholic potassium hydroxide solution into *ααδδ-tetraphenyl-Δ^{αβγ}-butatriene*, $CPh_2 \vdots C \vdots C \vdots CPh_2$, long, yellow needles, m. p. 240°; the latter is oxidised quantitatively by chromic acid in glacial acetic acid solution to carbon dioxide and benzophenone, and is reduced by sodium and amyl alcohol to ααδδ-tetraphenylbutane, m. p. 121° (cf. Valeur, A., 1903, i, 416), and by amyl alcohol and amalgamated zinc wool to ααδδ-tetraphenyl-Δ^{αγ}-butadiene, long, colourless needles, m. p. 202° (cf. Valeur, *loc. cit.*). It is converted by exposure to strong sunlight into the *hydrocarbon*, $(C_{28}H_{20})_2$, yellow crystals with green fluorescence, m. p. 280°, the investigation of which is not yet complete. Purdie and Arup (T., 1910, **97**, 1538) have described a substance, colourless crystals, m. p. 157—158°, which they obtained by the distillation of 2 : 2 : 5 : 5-tetraphenyl-2 : 5-dihydrofuran with zinc dust and considered to be ααδδ-tetraphenyl-Δ^{αβγ}-butatriene; this is not identical with the author's substance, and the reason for the difference has not been elucidated. A second *hydrocarbon*, orange-coloured platelets, m. p. 207—208°, to which the formula $C_6H_4 <^{CPh==}_{C(\vdots CPh_2)} > CH$ is ascribed provisionally,

is isolated from the mother-liquors obtained in the preparation of tetraphenylbutatriene; it is oxidised by chromic acid in boiling glacial acetic acid solution to carbon dioxide, benzophenone, and o-benzoylbenzoic acid. H. W.

Reduction of Organic Halogen Compounds. VI. $\alpha\alpha\delta\delta$-**Tetra-aryl-Δ^β-butinene.** K. BRAND (*Ber.*, 1921, **54**, [*B*], 2017—2021).—It has been shown previously (Brand, *Zeitsch. Elektrochem.*, 1910, **16**, 669) that $\beta\beta\beta$-trichloro-$\alpha\alpha$-diphenylethane is reduced in boiling alcoholic solution at a lead cathode to a compound, $C_4H_2Ph_4$, and later (Brand and Matsui, A., 1913, i, 1170), the similar p-tolyl and p-anisyl compounds have been prepared. At that time it was impossible to decide between the alternative formulæ, $CHPh_2 \cdot C\colon C \cdot CHPh_2$ and $CHPh_2 \cdot CH\colon C\colon CPh_2$, for the parent substance, since it is indifferent towards bromine and, on oxidation, gives relatively greatly varying amounts of benzophenone and diphenylacetic acid. The preparation of these compounds by the reduction of $\beta\beta\gamma\gamma$-tetrabromo-$\alpha\alpha\delta\delta$-tetraphenylbutane and $\beta\beta\gamma\gamma$-tetrabromo-$\alpha\alpha\delta\delta$-tetra-p-anisylbutane (preceding abstract and this vol., i, 787) leaves no doubt that they have the structure

$$CHAr_2 \cdot C\colon C \cdot CHAr_2.$$
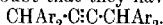
The unusual course of the oxidation of the phenyl derivative is explained by the observation that it yields $\alpha\alpha\delta\delta$-tetraphenyl-$\Delta^{\alpha\beta\gamma}$-butatriene when treated with calcium permanganate in well-cooled, aqueous pyridine solution : $CHPh_2 \cdot C\colon C \cdot CHPh_2 + O + H_2O \longrightarrow CHPh_2 \cdot C(OH)\colon C(OH) \cdot CHPh_2 \longrightarrow CPh_2\colon C\colon C\colon CPh_2$.

The author's previous assumption that the reduction of trichlorodiphenylethane to the butinene hydrocarbon occurs through the successive stages, $\beta\beta\gamma\gamma$-tetrachloro-$\alpha\alpha\delta\delta$-tetraphenylbutane, and $\beta\gamma$-dichloro-$\alpha\alpha\delta\delta$-tetraphenyl-Δ^β-butene, is rendered untenable by the observation that the latter substance is highly resistant to electrolytic reduction at a lead cathode. It now appears more probable that the primary action consists in the complete removal of chlorine from the ethane derivative, with formation of the radicles, $CHPh_2 \cdot C\colon$, which then unite in pairs with production of the butinene compound. H. W.

Keto-anils. I. Preparation of Aliphatic Keto-anils and Fission of Keto-anil Alkyliodides by Alkali. E. KNOEVENAGEL [with OTTO JÄGER] (*Ber.*, 1921, **54**, [*B*], 1722—1730).—A number of keto-anils have been prepared by the action of aromatic amines on aliphatic ketones in the presence of iodine. They are hydrolysed by acid with greater or less readiness, but are extremely stable towards alkali hydroxides. They combine readily with alkyl iodides, but the products formed are not the normal salts of quaternary ammonium bases, since, although they are stable towards hot acids, they are attacked readily by cold dilute alkalis, with the formation of substances which, according to analysis, are keto-anils into which the alkyl group has been introduced; pending the full elucidation of their constitution, it is proposed to term them 'alkylketo-anils.' Certain of the primary products of the action of alkyl iodides on keto-anils exhibit a gradual change in melting

point when preserved; this is explained by the hypothesis of isomerisation according to the scheme: $CMe_2:NMeI\cdot C_6H_4Me \rightarrow$

$$CH_2:CMe-NMe\cdot C_6H_4Me \quad \text{or} \quad Me_2C-N\cdot C_6H_4Me.$$
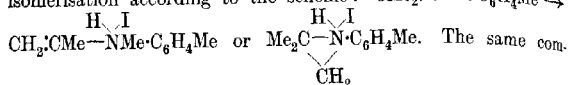
The same compound is obtained from either isomeride by the action of cold dilute alkali. The alkylketo-anils can also combine with alkyl iodide, giving normal quaternary ammonium iodides which are stable towards alkali and are transformed by silver oxide into the corresponding hydroxides; the latter lose alcohol when distilled and regenerate the alkylketo-anil.

The following individual substances are described : *Acetoneanil* (from the components and iodine under pressure at 180° or by protracted heating under a reflux condenser), a pale yellow liquid, b. p. 132°/13 mm., m. p. 23·5° [*hydrochloride*, m. p. 182—184°; *methiodide*, colourless crystals, m. p. 148°. *Methylacetoneanil*, a pale yellow liquid, b. p. 142°/13 mm., which yields a *hydrochloride*, m. p. 166—167°; a *hydriodide*, m. p. 139—141° and a *methiodide*, colourless crystals, m. p. 158° (decomp.)]. *Acetone-p-tolil*, a pale yellow liquid, b. p. 140°/11 mm., m. p. 36° [*methiodide*, m. p. 148° (decomp.), which rises when the substance is preserved during four weeks to 158°]. *Methylacetone-p-tolil*, a pale yellow liquid, b. p. 155°/14 mm. (*hydrochloride*, m. p. 164—165°; *hydriodide*, m. p. 80—82°; *methiodide*, colourless needles, m. p. 157·5—158·5°; *benzyliodide*, m. p. 198°). Acetone-*p*-tolil reacts with alkyl haloids with greatly varying velocity, yielding thus the *ethiodide*, colourless needles, m. p. 100—105°, n-*propiodide*, m. p. 116°, *benzylchloride*, m. p. 211—212°, and *benzyliodide*, m. p. 140—142°. *Benzylacetone-p-tolil* has m. p. 104—105°. *Acetone-o-tolil*, b. p. 138·5—139·5°/14 mm. (*hydrochloride*, m. p. 200—205°; *methiodide*, colourless crystals, m. p. 151°). *Acetone-m-tolil*, b. p. 143·5—144·5°/12 mm., m. p. 25°, (*hydrochloride*, m. p. 226—228°; methiodide, m. p. 159°). *Acetone-o-anisidil*, a glassy solid, b. p. 150—152°/13 mm. [*methiodide* (crude), m. p. 105—115°]. *Acetone-o-phenetidil*, m. p. 63° [methiodide (crude), m. p. 120—130°]. *Acetone-p-phenetidil*, a pale yellow liquid which solidifies to a vitreous mass, b. p. 169°/13 mm. (*methiodide*, m. p. 179°). *Methyl ethyl ketoanil*, b. p. 152—153°/14 mm. (*methiodide*, m. p. 208—211°, which when treated with dilute alkali gives a *liquid*, b. p. 157—164°/14 mm.).   H. W.

Manufacture of Alkylamides of Aromatic Sulphonic Acids.

BRITISH CELLULOSE AND CHEMICAL MFG. CO., LTD., WALTER BADER, and DONALD ARCHER NIGHTINGALE (Brit. Pat. 167941).— Aromatic sulphonalkylamides are obtained by the action of aromatic sulphonyl chlorides on alkylamine salts in presence of an alkali carbonate or other suitable acid neutralising agent, and a small quantity of water, preferably not exceeding 5% of the reaction mixture. For example, xylenesulphonmethylamide is obtained in almost theoretical yield by mixing together at 80—100° 1400 parts of xylenesulphonyl chloride, 470 parts of methylamine

hydrochloride, and 900 parts of sodium carbonate, the total moisture content not exceeding 5%. The product may conveniently be isolated by extraction with benzene followed by distillation in a vacuum.   G. F. M.

Reduction of Organic Halogen Compounds. V. Phenol Ethers of the Tetraphenylbutane Series. K. BRAND and FRANZ KERCHER (*Ber.*, 1921, **54**, [*B*], 2007—2017).—The observations recorded in the preceding paper (this vol. i, 783) have been extended to the corresponding pp'-dimethoxy- and pp'-diethoxy-derivatives. The behaviour of the former is exactly similar to that of the parent substances, whereas the latter pass mainly into pp'-diethoxystilbene.

$\beta\beta\beta$-Trichloro-$\alpha\alpha$-di-p-anisylethane is converted by Devarda's or Arndt's alloy in boiling alcoholic solution (the success of the method depends considerably on the water content of the alcohol) into $\beta\beta\gamma\gamma$-*tetrachloro-$\alpha\alpha\delta\delta$-tetra-p-anisylbutane*,

$$CH(C_6H_4 \cdot OMe)_2 \cdot CCl_2 \cdot CCl_2 \cdot CH(C_6H_4 \cdot OMe)_2,$$
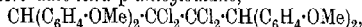
m. p. 204°, and dichlorotetra-anisylbutene. Under similar conditions, $\beta\beta\beta$-*tribromo-$\alpha\alpha$-di-p-anisylethane*, colourless needles, m. p. 113° (from bromal hydrate, anisole, and concentrated sulphuric acid in the presence of glacial acetic acid), yields $\beta\beta\gamma\gamma$-*tetrabromo-$\alpha\alpha\delta\delta$-tetra-p-anisylbutane*, small, coarse needles, m. p. 203° (decomp.). $\beta\beta\gamma\gamma$-Tetrachloro-$\alpha\alpha\delta\delta$-tetra-p-anisylbutane is reduced by zinc dust and boiling glacial acetic acid or, more slowly, by zinc dust and alcohol to the stereoisomeric $\beta\gamma$-*dichloro-$\alpha\alpha\delta\delta$-tetra-p-anisyl-Δ^β-butenes*, colourless needles, m. p. 129—130° and lustrous leaflets, m. p. 182°, respectively; the corresponding tetrabromo-derivative, on the other hand, is reduced to $\alpha\alpha\delta\delta$-tetra-p-anisyl-Δ^β-butinene, m. p. 110° (cf. Brand and Matsui, A., 1913, i, 1170). The stereoisomeric dichloro-compounds, m. p. 129—130° and 182°, respectively, are reduced by sodium and ethyl or amyl alcohol to $\alpha\alpha\delta\delta$-*tetra-p-anisyl-$\Delta^{\alpha\beta}$-butatriene*, $C(C_6H_4 \cdot OMe)_2 \cdot C \vdots C \cdot C(C_6H_4 \cdot OMe)_2$, long yellow or orange needles, m. p. 242°, and a *substance*, $C_{32}H_{28}O_4$, red needles, m. p. 173°, to which, by analogy with the corresponding compound derived from dichlorotetraphenylbutene (this vol. i, 783), the formula $OMe \cdot C_6H_3 \begin{subarray}{c} \diagdown \end{subarray} \begin{array}{l} C(C_6H_4 \cdot OMe) \text{---} \\ C[\vdots C(C_6H_4 \cdot OMe)] \end{array} \begin{subarray}{c} \diagup \end{subarray} CH$ is ascribed. The tetra-anisylbutatriene is oxidised by chromic acid in warm glacial acetic acid solution to carbon dioxide and pp'-dimethoxybenzophenone, m. p. 144°; it is reduced by sodium in boiling amyl alcoholic solution to $\alpha\alpha\delta\delta$-tetra-p-anisylbutane, m. p. 116° (cf. Brand and Matsui, *loc. cit.*), and by hydrogen and palladised charcoal to tetra-p-anisylbutadiene (cf. Brand and Matsui, *loc. cit.*) or the butane compound. $\alpha\alpha\delta\delta$-Tetra-p-anisyl-$\Delta^{\alpha\beta\gamma}$-butatriene is much more sensitive to light than the corresponding phenyl compound, and after comparatively short exposure becomes converted into a *substance*, $(C_{32}H_{28}O_4)_2$, greenish-yellow, strongly fluorescent crystals, m. p. 280°, and a smaller amount of a *product*, colourless needles, m. p. 286°, which has not yet been investigated further.

Reduction of $\beta\beta\beta$-trichloro-$\alpha\alpha$-di-p-phenetylethane by Devarda's

or Arndt's alloy gives a 2—3% yield of *pp'*-diethoxystilbene, m. p. 204—205°, together with small amounts of a substance, colourless needles, m. p. 146°, which is possibly dichlorotetraphenetylbutene, $C_{36}H_{38}O_4Cl_2$. Under similar conditions, *pp'*-diethoxystilbene is obtained from *ββββ-tribromo-αα-di-p-phenetylethane*, colourless needles, m. p. 119°; a compound, colourless needles, m. p. 180°, which is obtained simultaneously, may possibly be dibromotetraphenetyl-butene.   H. W.

Semipinacolic and Semihydrobenzoinic Transpositions in the α-Phenyl-β-methylpropane-αβ-diol Series. Action of Dilute Acids on the Glycol and its Oxide ; Elimination of HI from the Corresponding Iodohydrin. M. TIFFENEAU and A. ORÉKHOFF (*Bull. Soc. chim.*, 1921, [iv], **29**, 809—820).—A more detailed account of work already published (this vol., i, 243).
                                                                                    W. G.

Semipinacolic and Semihydrobenzoinic Transpositions in the Phenyldimethylglycol Series. Action of Concentrated Acids. (MLLE) JEANNE LÉVY (*Bull. Soc. chim.*, 1921, [iv], **29**, 820—829).—α-Phenyl-β-methylpropane-αβ-diol undergoes the semi-hydrobenzoinic transpositions with dilute acids, giving α-phenyl-α-methylpropaldehyde (cf. this vol., i, 243), but if concentrated acids are used the semipinacolic transposition, resulting in the formation of β-phenylbutanone, is produced. Thus dilute sulphuric acid and 50% oxalic acid produce the aldehyde, concentrated sulphuric acid gives the ketone, and phosphoric acid gives both the aldehyde and the ketone. Dimethylstyrene and its oxide behave in the same manner as the glycol in the presence of dilute and con-centrated acids respectively.   W. G.

The Phenylalanine Series. I. Synthesis of *l*-3 : 4-Dihydr-oxyphenylalanine. E. WASER and M. LEWANDOWSKI (*Helv. Chim. Acta*, 1921, **4**, 657—666).—Contrary to the statements of Funk (T., 1912, **99**, 1004), tyrosine may be nitrated without racemis-ation, and aminotyrosine may be diazotised. *l-3-Nitrotyrosine*, $C_9H_{10}O_5N_2$, m. p. 222—224 (decomp.), $[\alpha]_D^{15} +3\cdot21°$ (*hydrochloride*, radiate, yellow needles, m. p. 237°, decomp.), from *l*-tyrosine by nitration (Johnson and Kohmann, A., 1915, i, 899), on reduction (Funk, *loc. cit.*) yields *l-3-aminotyrosine*, needles, m. p. 287·5° (decomp.), $[\alpha]_D^{15} -3\cdot61°$ [hydrochloride, prisms, m. p. 175° (decomp.)]. The orientation of these compounds follows from the conversion in excellent yield of the amino-derivative into *l*-3 : 4-dihydroxyalanine, identical in all respects with the natural product, by adding the diazotised solution to boiling copper sulphate solution. *l-3 : 4-Dihydroxyphenylalanine hydrochloride* forms rosettes of prismatic crystals, m. p. 209°, decomp. 220°.   J. K.

Optically Active Bromohydroxy-β-phenylpropionic Acids. E. BERNER and C. N. RIIBER (*Ber.*, 1921, **54**, [B], 1945—1960; cf. A., 1917, i, 562).—The theoretically possible phenylbromo-

hydroxypropionic acids have been prepared and their relative configurations provisionally deduced. The following isomerides are possible.

$$
+ \quad
\begin{array}{c}
\text{Ph} \\
\text{H·C·Br} \\
\text{HO·C·H} \\
\text{CO}_2\text{H} \\
a.
\end{array}
\quad
\begin{array}{c}
\text{Ph} \\
\text{Br·C·H} \\
\text{H·C·OH} \\
\text{CO}_2\text{H} \\
b.
\end{array}
\quad - \qquad - \quad
\begin{array}{c}
\text{Ph} \\
\text{H·C·Br} \\
\text{H·C·OH} \\
\text{CO}_2\text{H} \\
a.
\end{array}
\quad
\begin{array}{c}
\text{Ph} \\
\text{Br·C·H} \\
\text{HO·C·H} \\
\text{CO}_2\text{H} \\
b.
\end{array}
\quad +
$$

(I.) (II.)

$$
+ \quad
\begin{array}{c}
\text{Ph} \\
\text{H·C·OH} \\
\text{Br·C·H} \\
\text{CO}_2\text{H} \\
a.
\end{array}
\quad
\begin{array}{c}
\text{Ph} \\
\text{HO·C·H} \\
\text{H·C·Br} \\
\text{CO}_2\text{H} \\
b.
\end{array}
\quad - \qquad + \quad
\begin{array}{c}
\text{Ph} \\
\text{H·C·OH} \\
\text{H·C·Br} \\
\text{CO}_2\text{H} \\
a.
\end{array}
\quad
\begin{array}{c}
\text{Ph} \\
\text{HO·C·H} \\
\text{Br·C·H} \\
\text{CO}_2\text{H} \\
b.
\end{array}
\quad -
$$

(III.) (IV.)
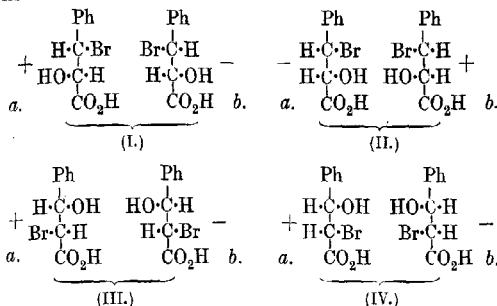
Phenylglyceric acid, m. p. 141°, is converted by aqueous hydrobromic acid solution, saturated at 0°, into r-β-bromo-α-hydroxy-β-phenylpropionic acid, monoclinic-prismatic or monoclinic-domatic crystals, $a : b : c = 1\cdot822 : 1 : 0\cdot999$, β=92° 42′, d 1·676, m. p. 165°. Similarly, d-phenylglyceric acid, m. p. 164°, yields d-β-bromo-α-hydroxy-β-phenylpropionic acid (Ia) whilst the l-acid (Ib) is similarly prepared from the corresponding glyceric acid; the optically active acids, m. p. 143°, d 1·700, form monoclinic sphenoidal crystals, $a : b : c = 1\cdot9862 : 1 : 0\cdot8564$. The l-acid has $[\alpha]_{D}^{20} - 122\cdot7°$, $[\alpha]_{D}^{20} - 95\cdot3°$, $[\alpha]_{D}^{20} - 161\cdot8°$ in 97·5 vol.% ethyl alcoholic solution ($p=3\cdot036$) and $[\alpha]_{D}^{20} - 114\cdot92°$ ($p=1\cdot05$); the specific rotation diminishes with increasing temperature. The d-acid has $[\alpha]_{D}^{20} +122\cdot9°$ in ethyl alcohol ($p=2\cdot48$) and $[\alpha]_{D}^{20} +116\cdot0°$ in acetone. One hundred grams of chloroform dissolve 0·30, 1·00, and 1·00 gram of the r-, d-, and l-acids respectively at 20°. A 3% solution of the r-, d-, and l-acids in ethyl alcohol (99·80 vol. per cent.) has d_{20}^{20} 0·8047, 0·8046, and 0·8047 respectively. Reduction of the bromo-acids by means of sodium amalgam in acidified alcoholic solution gives the α-hydroxy-β-phenylpropionic acids; a change in the direction of rotation does not occur in the cases of the optically active acids. The configuration Ia is assigned to the d-acid on account of its relationship to d-phenylglyceric acid, to which the annexed formula is assigned arbitrarily, the assumption being made that configurational change does not occur during the replacement of hydroxyl by bromine.

$$
\begin{array}{c}
\text{Ph} \\
\text{H·C·OH} \\
\text{HO·C·H} \\
\text{CO}_2\text{H}
\end{array}
$$

r-Phenylglyceric acid, m. p. 122°, is converted by hydrobromic acid solution into r-β-bromo-α-hydroxy-β-phenylpropionic acid, m. p. 157°, d 1·674, monoclinic-prismatic or monoclinic-domatic crystals, $a : b : c = 1\cdot814 : 1 : 0\cdot976$, β=93° 21′. Similar treatment of the active phenylglyceric acids yields the optically active *β-bromo-α-hydroxy-β-phenylpropionic acids*, reaction being accompanied by change in the direction of rotation. The latter form monoclinic,

sphenoidal crystals, $a : b : c = 1.9840 : 1 : 0.8543$, $\beta = 94°$ 5′, m. p. 138°; the l-acid has $[\alpha]_D^{20} -121.7°$, $[\alpha]_C^{20} -94.2°$, $[\alpha]_E^{20} -160.1°$ in ethyl alcohol (97·5 vol. %) and $[\alpha]_D^{20} -113.4°$ in acetone. The d-acid has $[\alpha]_D^{20} +122.3°$ ($p = 2.888$) and $+117.6°$ ($p = 1.444$) in alcohol; the specific rotation diminishes with increasing temperature. One hundred grams of chloroform dissolve 0·20, 2·60, and 2·60 grams of the r-, d-, and l-acids respectively at 20°. The configuration IIb is assigned to the d-acid, since, on reduction with sodium amalgam, it yields the same d-α-hydroxy-β-phenylpropionic acid as is obtained from the acid Ia.

. r-α-Bromo-β-hydroxy-β-phenylpropionic acid is prepared by boiling dibromocinnamic acid with water or by the addition of hypobromite to cinnamic acid. Under suitable condition, it can be isolated in two dimorphous forms, the α-modification, m. p. 125°, d 1·697, consisting of monoclinic crystals, $a : b : c = 1.0099 : 1 : 1.1875$, $\beta = 126°$ 45′, whereas the β-*modification* forms rhombic crystals, d 1·691, $a : b : c = 0.7067 : 1 : 1.2963$. The former modification is stable at the atmospheric temperature, whereas the latter is labile. The optically active acids are prepared by resolution of the r-acid by cinchonine (cf. Barkow, *Diss. Mannheim*, 1906) or by treatment of the active dibromosuccinic acids with water; contrary to the observations of Barkow (*loc. cit.*), the latter reaction occurs without change in the sign of rotation. The d-acid forms monoclinic-sphenoidal crystals, $a : b : c = 0.635 : 1 : 0.697$, $\beta = 104°$ 38′, m. p. 119°, d 1·736; it has $[\alpha]_C^{20} +15.6°$, $[\alpha]_D^{20} +20.2°$, $[\alpha]_E^{20} +26.4°$, $[\alpha]_F^{20} +32.4°$ ($p = 3.01$), and $[\alpha]_D^{20} +19.5°$ ($p = 1.53$) in ethyl alcohol (99·75 vol. %); the specific rotation increases with rise in temperature. The values, m. p. 116°, $[\alpha]_D^{20} -18.2°$, in absolute alcohol were found for the l-acid. One hundred grams of chloroform dissolve 0·30, 0·66, and 0·37 gram of the $r(\alpha)$-, $r(\beta)$-, and d-acids respectively at 20°. A 3% solution of the r-acid in alcohol has d_{20}^{20} 0·8047. Reduction of the α-bromo-β-hydroxy-β-phenylpropionic acids by sodium amalgam leads to the formation of the β-hydroxy-β-phenylpropionic acids, and is not accompanied by change in the direction of rotation in the cases of the optically active acids. Treatment of the r-acid, m. p. 125°, with hydrobromic acid gives dibromocinnamic acid, m. p. 195°, whereas the d-acid yields d-dibromocinnamic acid, m. p. 182°, $[\alpha]_D^{18} +45.8°$, thus pointing to the configuration IIIa for the d-acid.

r-α-*Bromo-β-hydroxy-β-phenylpropionic acid*, m. p. 69° (formula group IV), cannot be prepared by the treatment of *allo*cinnamic acid dibromide with boiling water (which gives the stable acid, III, m. p. 125°), but results from the addition of hypobromite to potassium *allo*cinnamate solution; it forms rhombic, probably bipyramidal, crystals, $a : b : c = 0.6602 : 1 : 1.2694$, d 1·724. The active *components* are produced by the resolution of the r-acid by means of strychnine in methylal solution and form monoclinic-sphenoidal crystals, $a : b : c = 1.1055 : 1 : 0.8749$, $\beta = 113°$ 2′, m. p. 97°; the l-acid has $[\alpha]_C^{20} -8.25°$, $[\alpha]_D^{20} -9.39°$, $[\alpha]_E^{20} -10.44°$ in ethyl alcohol (99·80 vol. %) for $p = 2.30$ and $[\alpha]_D^{20} -13.06°$ ($p = 0.86$). The values, m. p. 93—94°, $[\alpha]_D^{20} +7.81°$, in alcohol ($p = 2.31$) are

recorded for the d-acid. One hundred grams of chloroform dissolve 0·51 and 1·77 grams of the r- and d-acids respectively at 20°. A 3% solution of the r-acid in alcohol has d_{20}^{20} 0·8045. Reduction of the acids by sodium amalgam gives the β-hydroxy-β-phenylpropionic acids, the action being accompanied by a change in the direction of rotation in the cases of the optically active acids. Treatment of the r-acid, m. p. 69°, with hydrobromic acid gives cinnamic acid dibromide, m. p. 195°, in place of the expected *allo*-dibromide under similar conditions, the l-acid, m. p. 97°, yields a dextrorotatory mixture of cinnamic acid dibromides.

The methyl esters of the r-phenylglyceric acids, m. p. 141° and . 122°, are converted by phosphorus pentabromide at a temperature not exceeding 80° into methyl dibromocinnamate, m. p. 117°. The dextrorotatory component of phenylglyceric acid, m. p. 141°, when esterified with diazomethane and treated with phosphorus pentabromide, yields methyl dibromocinnamate, m. p. 114°, $[\alpha]_D$ +22·9°; change of sign of rotation is not observed when the optically active dibromocinnamic acids are esterified with diazomethane. H. W.

The Fluorene Series. VI. A. SIEGLITZ and H. JASSOY (*Ber.*, 1921, **54**, [*B*], 2133—2138).—*Ethyl fluorene-9-glycollate,*

$$\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} {>} CH{\cdot}CH(OH){\cdot}CO_2Et,$$
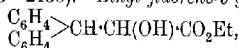
colourless rods, m. p. 81—82°, is obtained by the reduction of a solution of ethyl fluorene-9-glyoxylate in moist ether with aluminium amalgam and is transformed by boiling sodium ethoxide solution into *dibenzofulvene-ω-carboxylic acid,* $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} {>} C{:}CH{\cdot}CO_2H,$ yellow needles, m. p. 227—228° (decomp.), *methyl* ester, lustrous yellow needles, m. p. 112—113°, *ethyl* ester, which is more conveniently prepared from fluorenone, ethyl bromoacetate, and zinc in boiling·benzene solution, b. p. 248°/13 mm., m. p. 77°. The unsaturated ester is reduced quantitatively to ethyl fluorene-9-acetate which, when treated with hydrazine hydrate in boiling alcoholic solution, gives the corresponding *hydrazide,* colourless needles, m. p. 188° (*benzylidene* derivative, colourless, slender needles, m. p. 192°). The latter is converted in the usual manner into the *azide,* decomp. 67—68°, and *urethane,* long, colourless needles, m. p. 112—113°. Conversion of the urethane into 9-aminomethylfluorene could not be effected with concentrated hydrochloric acid, sulphuric acid (50%), or concentrated ammonia; by distillation with lime, however, a reddish-yellow, unstable liquid, presumably the crude amine, was isolated, which rapidly loses ammonia when preserved in contact with air or treated with solvents, and yields a solid substance, (?) dibenzofulvene.

The following compounds are obtained by the reduction of the corresponding fulvenes with aluminium amalgam : 9-*o-methylbenzylfluorene,* colourless cubes, m. p. 71—72°; 9-*p-methylbenzylfluorene,* colourless crystals, m. p. 136—137°; 9 : 9′-*m-xylylenedifluorene,* needles, m. p. 119—120°; 9 : 9′-*p-xylylenedifluorene,*

colourless rods, m. p. 239—240°; 9-o-*chlorobenzylfluorene*, colourless leaflets, m. p. 67—68°; 9-m-*chlorobenzylfluorene*, colourless needles, m. p. 122—123°; 9-p-*chlorobenzylfluorene*, long, colourless spikes, m. p. 150—151°; 9-m-*bromobenzylfluorene*, colourless leaflets, m. p. 143—144°; 9-m-*iodobenzylfluorene*, feathery leaflets, m. p. 134—135°.

9-α-*Naphthylmethylfluorene*, colourless rods, m. p. 133—134°, and 9-β-*naphthylmethylfluorene*, m. p. 164°, are prepared from ethyl fluoreneglyoxylate and naphthylmethyl bromide.   H. W.

The Fluorene Series. IV. Synthesis of *iso*Diphenic Acid. A. SIEGLITZ and J. SCHATZKES (*Ber.*, 1921, **54**, [B], 2070—2071).— It has been shown recently by Mayer and Freitag (this vol., i, 248) that Fittig's *iso*diphenic acid is diphenyl-2 : 3'-dicarboxylic acid. Its constitution is further confirmed by its production from fluoren-one-3-carboxylic acid.

3-Methylfluorenone, m. p. 68°, is prepared from toluene, toluene-*p*-sulphonyl chloride, and anthranilic acid, and is oxidised by boiling potassium permanganate solution to *fluorenone-3-carboxylic acid*, yellow, crystalline aggregates, m. p. 285—286°; the latter is trans-formed by molten potassium hydroxide into *iso*diphenic acid, m. p. 213—214° after softening at 195°.   H. W.

Colophenic Acid. W. FAHRION (*Ber.*, 1921, **54**, [B], 1944).— In his recent publication (this vol., i, 512), Aschan appears to have overlooked the author's work on the autoxidation of colophony (A., 1907, i, 329). Aschan's colophenic acid is apparently identical with oxyabietic acid.   H. W.

The Mechanism of the Action of Fused Alkalis. II. The Action of Fused Potassium Hydroxide on Phenylglyceric Acid. (The late) HENRY RONDEL LE SUEUR and CYRIL CHRISTIAN WOOD (T., 1921, **119**, 1697—1700).

ψ-Tetrahydroanemonic Acid. ATSUSHI FUJITA (*J. Pharm. Soc. Japan*, 1921, 679—691).—By warming ḍ-tetrahydroanemonic acid (cf. *ibid.*, 1919, 739) with hydrogen iodide or by boiling tetra-hydroanemonin with hydrogen iodide (*d* 1·7), *ψ-tetrahydroanemonic acid hydriodide*, $C_{10}H_{15}O_5I$, white prisms, m. p. 124°, is obtained; it is unstable and changes ḷto ψ-tetrahydroanemonic acid when warmed with dilute alkali or boiled with water. On reduction with zinc and hydrochloric acid, the hydriodide produced an iodine-free acid, "*acetoneaceticvaleric*" [? γ-*keto-octane-αθ-dicarboxylic*] acid, $C_{10}H_{16}O_5$, white needles, m. p. 90° (*semicarbazone*, white prisms, m. p. 148°). From the semicarbazone, sebacic acid was isolated by Wolff's method of reduction (*Annalen*, 1866, **139**, 86). When heated with methyl alcohol and concentrated sulphuric acid, ψ-tetrahydroanemonin yields *methyl-ψ-tetrahydroanemonate*, a colour-less oil, b. p. 184—185°/13 mm., produced also from ψ-tetrahydro-anemonic acid by the same treatment; the ester yields ψ-tetra-

hydroanemonic acid on hydrolysis with cold alkali. ψ-Tetra-hydroanemonic acid has probably one of the two formulæ

$$CH_2 \cdot C\colon CH \cdot CH_2 \cdot CO_2H$$
$$\big|\ \ \ \big\rangle O$$
$$CH_2 \cdot CH \cdot CH_2 \cdot CH_2 \cdot CO_2H$$

or

$$CH_2 \cdot C \cdot CH_2 \cdot CH_2 \quad (O\text{—}CO)$$
$$\big|\ \ \ \big\rangle O$$
$$CH_2 \cdot CH \cdot CH_2 \cdot CH_2 \cdot CO_2H.$$
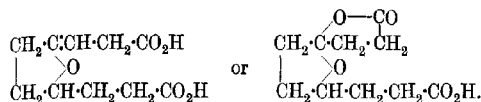
<div align="right">K. K.</div>

Constitution of the Peppermint Ketone of Eucalyptus Oils. L. GIVAUDAN & Co. (*Perf. Essent. Oil Rec.*, 1921, **12**, 80—81; *cf.* Smith and Penfold, *J. Roy. Soc. New South Wales*, 1920, **54**, 40).—Since by oxidation piperitone yields 2-hydroxy-Δ^1-menthen-3-one, it must have the constitution $CMe\!\!<^{CH \cdot CO\text{---}}_{CH_2 \cdot CH_2}\!\!>\!CH \cdot CHMe_2$.

<div align="right">CHEMICAL ABSTRACTS.</div>

Reactivity of Doubly-conjugated Unsaturated Ketones. I. 4′-Dimethylamino-2-hydroxydistyryl Ketone. ISIDOR MORRIS HEILBRON and JOHANNES SYBRANDT BUCK (T., 1921, **119**, 1500—1515).

Reactivity of Doubly-conjugated Unsaturated Ketones. II. The Action of Hydroxylamine, Semicarbazide, and Phenylhydrazine on 4′-Dimethylamino-2-hydroxydistyryl Ketone and its Methyl Ether. ISIDOR MORRIS HEILBRON and JOHANNES SYBRANDT BUCK (T., 1921, **119**, 1515—1520).

Hydroxycarbonyl Compounds. VI. Phloroglucinol and Resorcinol Ketones. P. KARRER and S. ROSENFELD (*Helv. Chim. Acta*, 1921, **4**, 707—717; *cf.* this vol., i, 341).—An extension of previous work (A., 1919, i, 592). *Phloroisobutyrophenone*, m.,p. 138—140°, forms a *dihydrate*, $C_6H_2(OH)_3 \cdot CO \cdot CHMe_2, 2H_2O$, m. p. 68°, and gives a brownish-red colour with ferric chloride. *Phloro-isovalerophenone*, $C_6H_2(OH)_3 \cdot CO \cdot CH_2 \cdot CHMe_2$, m. p. 178°, *mono-hydrate*, m. p. 95°, colours ferric chloride brownish-red. *Phloro-isohexophenone*, $C_6H_2(OH)_3 \cdot CO \cdot [CH_2]_2 \cdot CHMe_2$, m. p. 122°, *monohydrate*, m. p. 104°, colours ferric chloride brownish-red. *Phloroenanthophenone*, $C_6H_2(OH)_3 \cdot CO \cdot [CH_2]_4 \cdot CH_2Me$, m. p. 107°, *monohydrate*, m. p. 98—100°. *Phloro-octophenone*, m. p. 124°, *monohydrate*, $C_6H_2(OH)_3 \cdot CO \cdot [CH_2]_5 \cdot CH_2Me, H_2O$, m. p. 106°. *Phloro-stearophenone*, $C_6H_2(OH)_3 \cdot CO \cdot [CH_2]_{15} \cdot CH_2Me$, m. p. 126—127°, colours ferric chloride brownish-red. *Resobutyrophenone*, $C_6H_3(OH)_2 \cdot COPr$, m. p. 70°; *hemihydrate*, m. p. 51—52°. *Reso-isohexophenone*, $C_6H_3(OH)_2 \cdot CO \cdot [CH_2]_2 \cdot CHMe_2$, m. p. 83—84°, colours ferric chloride brownish-red. *Resoenanthophenone*, $C_6H_3(OH)_2 \cdot CO \cdot [CH_2]_4 \cdot CH_2Me$, m. p. 49°, *hemihydrate*, m. p. 43°, reacts similarly with ferric chloride. *Reso-octophenone*, $C_6H_3(OH)_2 \cdot CO \cdot [CH_2]_5 \cdot CH_2Me$, m. p. 59°, *hemihydrate*, m. p. 58°. *Methylphloroisohexophenone*, $C_6HMe(OH)_3 \cdot CO \cdot [CH_2]_2 \cdot CHMe_2$, m. p. 156°. *Methylphloroenanthophenone*, $C_6HMe(OH)_3 \cdot CO \cdot [CH_2]_4 \cdot CH_2Me$, m. p. 143—144°, forms a monohydrate. *Methylphloro-octophenone*, $C_6HMe(OH)_3 \cdot CO \cdot [CH_2]_5 \cdot CH_2Me$, m. p. 135°, forms a monohydrate.
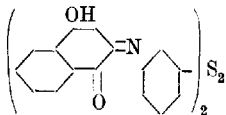
A comparative study of these compounds as remedies against the tape-worm showed that the resorcinol may replace the phloro-glucinol residue, and that other acid residues are equally as effective as the butyryl and *iso*butyryl groups, the *iso*hexoyl residue being the most valuable.   J. K.

Action of o-Aminothiophenol on Orthoquinones. III. KNUT STAHRFOSS (*Helv. Chim. Acta*, 1921, **4**, 644—657).—Besides the two products of the condensation of *o*-aminothiophenol and 4-amino-β-naphthaquinone in presence of acetic acid already described (this vol., i, 457), a third is obtained as a sparingly soluble potassium salt by extraction of the precipitate resulting from the dilution of the acetic acid solution, with boiling 3% potassium hydroxide solution. The new compound forms brown needles, and is shown to be the *disulphide* (annexed formula) corresponding with *o-thiolphenyl*-4-*hydroxy-β-naphthaquinone-2-imide*. This formula is confirmed by syntheses of the compound from *o*-aminothiophenol and 4-hydroxy-β-naphtha-quinone and from 2 : 2′-diaminodiphenyl disulphide and 2-amino-α-naphthaquinone. It cannot be obtained from β-naphthaquinone-4-sulphonic acid (cf. Böniger, A., 1894, i, 199) or from 4-amino-β-naphthaquinone. It is therefore formed in the above condensation by a preliminary reaction corresponding with the formation of *o*-hydroxyanilino-α-naphthaquinone (Kehrmann, A., 1895, i, 245) from *o*-aminophenol and 4-hydroxy-β-naphthaquinone, followed by replacement of an amino- by a hydroxyl-group (D.R.P. 97675) and oxidation of the thiophenolic group at the expense of the aminoquinone. The formula also explains the salt-formation, and the fact that the compound does not condense with *o*-aminophenol or *o*-phenylenediamine.   J. K.

o-Dimethylanthraquinones and their Derivatives. ARTHUR FAIRBOURNE (T., 1921, **119**, 1573—1582).

2-Aldehydoanthraquinone. WERNER JACOB (*Helv. Chim. Acta*, 1921, **4**, 782—788).—Condensation products of 2-alde-hydoanthraquinone (p-*nitrophenylhydrazone*, $C_{21}H_{13}O_4N_3$, leaflets, m. p. 305—306°) with compounds containing a reactive methylene group have been prepared as follows : with acetophenone, $C_{23}H_{14}O_3$, needles, m. p. 241—242°; with 1-hydroxy-2-methyl ketone, $C_{27}H_{16}O_4$, reddish-yellow needles, m. p. 296—297° (*methyl ether*, $C_{28}H_{18}O_4$, yellow leaflets, m. p. 214—215°); with 1-hydroxy-4-naphthyl methyl ketone, $C_{27}H_{16}O_4$, yellow needles, m. p. 226—227° (*methyl ether*, $C_{28}H_{18}O_4$, yellow needles, m. p. 228—229°); with coumaranone, $C_{23}H_{12}O_4$, yellow needles, m. p. 309—310°; with 6-methoxycoumar-anone, $C_{24}H_{14}O_5$, yellow needles, m. p. 280—282°; with α-naphtha-coumaranone, $C_{27}H_{14}O_4$, yellow needles, m. p. 223—225°; with 5-bromoindanone, $C_{24}H_{13}O_3Br$, yellowish-green leaflets, m. p. 299—300°; with indandione, $C_{24}H_{12}O_4$, greenish-yellow needles, m. p. 300—301°.   J. K.

tert.-Pinene **Hydrochloride. The Pinacolin Trans-**
formation. OSSIAN ASCHAN (*Öfvers. Finska Vet.-Soc.*, 1914,
57, [4], No. 1, 35 pp.; from *Chem. Zentr.*, 1921, iii, 629—631).—
The action of dry hydrogen chloride on pinene (I) at low tem-
peratures does not give ordinary pinene hydrochloride (bornyl
chloride) (II), but an isomeric liquid compound, *tert.-pinene hydro-
chloride* (III). This compound differs from bornyl chloride in
that it contains the bicyclic tetrocean system of pinene and
decomposes partly on treatment with aniline, giving hydrogen
chlorides and a pinene which is optically active in the same sense
as the original material. The elimination of hydrogen chloride takes
place with development of heat, *tert.*-pinene hydrochloride being
stable only below −10°. In the absence of cooling, the temperature
rises to 60—80° with transformation into solid bornyl chloride (II).
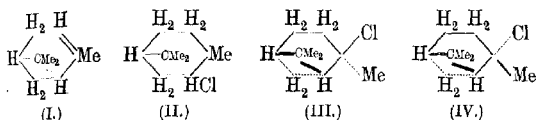
It is supposed that in the formation of bornyl chloride from pinene
and hydrochloric acid (pinacolin transformation) the unstable
compound (III) occurs as an intermediate product.

Nopinene forms with hydrogen chloride the same tertiary pinene
hydrochloride (III) as is given by ordinary pinene with aniline. The
change from nopinene to ordinary pinene by way of the compound
III takes place more directly and simply than the change by way
of nopinic acid ⟶ nopinone ⟶ nopinolacetic acid (Wallach, A.,
1909, i, 706). No verifiable amount of nopinene is formed in the
decomposition above mentioned. The compound, $C_{10}H_{17}Cl$,
obtained by Wallach by the action of phosphorus pentachloride
on methyl nopinol is probably a stereoisomeride of the compound
III and may have the constitution represented by formula IV.
(The thick lines are supposed to be above and the dotted lines
below the plane of the paper in formulæ III and IV). The rate
of transformation of tertiary pinene hydrochloride is greater than
its rate of formation from pinene and hydrogen chloride above 0°,
and even at low temperatures it cannot be obtained free from
bornyl chloride. It has a suffocating odour and attacks the
mucous membrane strongly. The saturation of the original hydro-
carbon with dry hydrogen chloride was carried out at −15° with
the addition of 4 to 10% of ether. On adding to the hydrochloride
an equal volume of aniline and leaving it at the ordinary tem-
perature, the transformation sets in quickly and the temperature
of the mixture rises above 80°. When the temperature falls again
the mixture is heated for about four hours on a water-bath. Glacial
acetic acid is added to fix the excess of aniline and volatile products
are removed by steam distillation. The principal product is
bornyl chloride. The mixture of hydrocarbons resulting from its
decomposition consists essentially of ordinary pinene, but contains

some dipentane and limonene. The fraction distilling over between 162° and 167° appears to contain an unknown bicyclic terpene. Using pinene from different sources with varying optical rotations, different results were obtained both for the yield of bornyl chloride and of regenerated pinene.   G. W. R.

**Conversion of Pinene Compounds into a Mixture of *iso*-Bornyl Ester and Camphene.** L. G. WESSON (U.S. Pat. 1372382). —Pinene hydrochloride is mixed with glacial acetic acid in the proportions of 100 to 300 parts, a small quantity of rather coarse zinc powder (preferably about 2 parts) is added after the mixture has been heated to vigorous boiling under a reflux condenser, and the boiling is continued for about eighteen hours. The zinc slowly dissolves and a large proportion of the hydrogen chloride is evolved and recovered. After about eighteen hours, the mixture usually contains about 83—85 parts of *iso*bornyl acetate, 10 parts of camphene, 5 parts of camphene hydrochloride, and 10 parts or less of unconverted pinene hydrochloride. A mixture of *iso*bornyl acetate, camphene, and camphene hydrochloride is separated by fractional distillation in a vacuum and this mixture may be employed for the production of synthetic camphor. The use of such a small amount of zinc and the avoidance of unduly high temperatures or more prolonged heating obviate the formation of any considerable quantity of resinous substances. Instead of acetic acid, formic, propionic, stearic, benzoic, or salicylic acid or other acid may be used and instead of pinene hydrochloride the hydrobromide or hydrofluoride is suitable for carrying out similar reactions.

CHEMICAL ABSTRACTS.

Pinene. IV. Synthesis of Pinocamphone and α-Pinene from Monocyclic Compounds. L. RUZICKA and H. TREBLER (*Helv. Chim. Acta*, 1921, **4**, 666—678; cf. this vol., i, 573).—By condensation of ethyl *r*-pinate with ethyl chloroacetate in presence of sodium ethoxide (Darzens, A., 1905, i, 116) or, much less effectively, of sodamide (Claisen, A., 1905, i, 286), the *glycidic ester*, $C_{16}H_{26}O_5$, b. p. 140—150°/0·3 mm., is obtained. The corresponding *acid*,

$$CO_2H \cdot CH_2 \cdot CH {<}^{CMe_2}_{CH_2}{>} CH \cdot CMe {<}^{CH \cdot CO_2H}_{O}, \quad m. p. 128° \text{ (decomp.)},$$

is converted at 230° in a vacuum into the *semialdehyde* of *homopino-camphoric acid*,

$$CO_2H \cdot CH_2 \cdot CH {<}^{CMe_2}_{CH_2}{>} CH \cdot CHMe \cdot CHO, \quad b. p.$$

130—140°/0·3 mm. [*semicarbazone*, $C_{12}H_{21}O_3N_3$, m. p. 193—195° (decomp.)], from which *homopinocamphoric acid*,

$$CO_2H \cdot CH_2 \cdot CH {<}^{CMe_2}_{CH_2}{>} CH \cdot CHMe \cdot CO_2H,$$
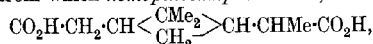
is obtained, and converted through its silver salt into its *diethyl ester*, $C_{15}H_{26}O_4$, b. p. 130°/1 mm., 120°/0·2 mm. *r*-Pinocamphone, identical with that derived from pinene, is best obtained from homopinocamphoric acid by subjecting its diethyl ester to the Dieckmann reaction, and hydrolysing the product with acid, much less satisfactorily by heating the acid with acetic anhydride (Blanc,

A., 1907, i, 710), and not at all by distillation of the lead salt. The conversion of the ketone into α-pinene has already been achieved (this vol., *loc. cit.*; Tschugaev, A., 1908, i, 93). The expansion of this partial into a total synthesis is discussed. J. K.

Chemistry of the Terpenes. XX. The Action of Hypochlorous Acid on Pinene. GEORGE GERALD HENDERSON and JOSEPH KENNETH MARSH (T., 1921, **119**, 1492—1500).

The Olibanols. EMIL FROMM and RICHARD KLEIN (*Annalen*, 1921, **425**, 208—216).—Pure pinene when oxidised by cold permanganate gives pinonic acid (isolated as its *semicarbazone*, m. p. 204°), but no pinononic acid, the production of which by Wagner and Erschtschikowski (A., 1896, i, 380) must be attributed to the presence of verbinone or some analogous substance in the pinene they employed. Olibanol (Fromm and Autin, A., 1914, i, 70), when isolated from oil of frankincense by distillation in a vacuum, has b. p. 117—119°/22 mm., and also yields no pinononic acid. It is called α-*olibanol* to distinguish it from the isomeride, β-*olibanol*, into which it is converted on distillation at atmospheric pressure (b. p. 210—211°), which yields pinononic acid on oxidation. α-Olibanol, on reduction by sodium and alcohol, gives *dihydro-olibanol*, $C_{10}H_{18}O$, b. p. 100—102°/25 mm., which has an odour resembling sage and appears to be an alcohol. It was characterised by a crystalline o-*nitrobenzoate*, m. p. 135—137°. β-Olibanol does not show these properties. Another isomeride, γ-*olibanol*, b. p. 114—116°/15 mm., $d^{18} = 0.9502$, isolated from a different specimen of oil of frankincense, gives no dihydro-compound, and does not yield β-olibanol on distillation. On oxidation, it gives a liquid acid from which no semicarbazone can be obtained. C. K. I.

Physical Constants and Characteristic Derivatives of the Principal Constituents of the Essential Oils. (*Roure-Bertrand fils Sci. Ind. Bull.*, 1920, [4], No. 2, 37—48).—A table is given showing the physical constants and characteristic derivatives of the principal aldehydes found in essential oils, namely: aromadendral, myrtenal, dihydrocuminaldehyde, citral, neral, phellandral, citronellal, *nor*-tricycloekasantalal, santalal, farnesal; formaldehyde, acetaldehyde, butaldehyde, valeraldehyde, *iso*valeraldehyde, *n*-hexaldehyde, *n*-octaldehyde, *n*-nonaldehyde, decaldehyde, lauraldehyde, benzaldehyde, phenylacetaldehyde, cumaldehyde, cinnamaldehyde, salicylaldehyde, anisaldehyde, o-methoxycinnamaldehyde, *p*-methoxycinnamaldehyde, vanillin, piperonaldehyde, furfuraldehyde, and 2-methylfurfuraldehyde. CHEMICAL ABSTRACTS.

The Essential Oil from *Andropogon iwarancusa*, Jones, **and the Constitution of Piperitone.** JOHN LIONEL SIMONSEN (T., 1921, **119**, 1644—1654).

Certain Essential Oils. (*Roure-Bertrand Fils Sci. Ind. Bull.*, 1920, [4], No. 2, 29—37).—Oil of chenopodium : By steam distillation, 0.7% of a light-yellow oil was obtained from chenopodium seed obtained from the Dutch East Indies. Its analytical constants

are: d^{15} 0·9763; $[\alpha]_D^{15}$ ±0°; acid number 0·93; saponification number 7·47; ester number 6·54; solubility in 70% alcohol, 2 vols. and over. By extracting the distilled waters with light petroleum, an additional 0·35% of oil was obtained possessing the following characters: d^{15} 0·9843; $[\alpha]_D^{15}$±0°; acid number 0·93; saponification number 13·98; ester number 13·05; soluble with difficulty in 70% alcohol. The optical rotation of these oils differentiates them from the American oil which has $[\alpha]_D$ —4° to —3° 30'. Oil of *Skimmia laureola*: A sample of oil distilled from the herb of *Skimmia laureola*, Hook showed: d^{18} 0·8931; $[\alpha]_D^{18}$+4° 28'; acid number 0; saponification number 82·13; soluble in 3 volumes of 90% alcohol. Oil of cinnamon from Annam : a sample gave : d^{15} 1·051; n_D 1·6090; $[\alpha]_D$—0° 8'; acid number 2·8; aldehyde content 95%; solubility in 70% alcohol, one volume and over. The odour of the oil is more pungent and less fine than that of oil of Ceylon cinnamon. It resembles a rectified Chinese oil of good quality in its characters.

CHEMICAL ABSTRACTS.

Labdanum and the Analytical Characters of the Oils of Cistus Ladaniferus, L., and Cistus monspeliensis, L. (*Roure-Bertrand Fils Sci. Ind. Bull.*, 1920, [4], No. 2, 25—29).—Analytical data obtained by Pelletier and by Guibourt for labdanum are given, also data of a similar nature by Parry ("Chemistry of Essential Oils," vol. 1, p. 503) and Masson (A., 1912, i, 280) for the oil distilled from the oleoresin. The author obtained 0·06% of a golden-yellow oil by steam distillation from the oleoresin extracted from *Cistus ladaniferus* L. This oil possessed the following characters: d^{20} 0·9033; $[\alpha]_D^{17}$—12° 10'; $n_D^{17.5}$ 1·4800; acid number 3·7; saponification number 22·37; ester number 18·67; solubility in 90% alcohol 0·5 to 5 volumes. The extraction of the distilled waters with light petroleum yielded an additional 0·02% of oil with the following characters : $d^{17.5}$ 0·9755; $[\alpha]_D^{17}$ —2° 40'; acid number 18·67; saponification number 41·07; ester number 22·40; solubility in 90% alcohol 0·5 vol. and over. Data obtained by Schimmel and Co., (*Semi-Ann. Rept.*, 1903, October, p. 81) for the oil obtained from *Cistus monspeliensis* are also given.   CHEMICAL ABSTRACTS.

Presence of Manganese in Raw Caoutchouc and the Origin of Tackiness. G. BRUNI and C. PELIZZOLA (*Atti R. Accad. Lincei*, 1921, [v], **30**, ii, 37—41).—When kept at the ordinary temperature, a mixture of caoutchouc with 1% of colloidal manganese dioxide very soon becomes tacky and in a few weeks almost liquid. The number of milligrams of manganese per 100 grams of caoutchouc has been found to vary from 0·0625 to 0·250 with the sound material, from 3·75 to 20 for samples showing uniform and profound tackiness, and from 0·625 to 3·75 for slightly and irregularly tacky samples. The manganese probably causes catalytic oxidation of the caoutchouc.   T. H. P.

Anemonin Derivatives. YASUHIKO ASAHINA and ATSUSHI FUJITA (*J. Pharm. Soc. Japan*, 1921, 331—335; cf. A., 1920, i, 70, 321, 493, 678; this vol., i, 792).—When reduced with sodium amalgam

ınd acetic acid at the ordinary temperature, anemonin yields mainly lihydroanemonin and a small quantity of a substance having n. p. 98°, whilst the latter only is produced by using boiling methyl ılcohol as solvent. When heated with hydriodic acid, the sub-ıtance, m. p. 98°, yields anemonolic acid, and therefore is proved to ɔe dimethyl anemonolate. iso*Tetrahydroanemonin*, m. p. 142°, ıs produced by reducing anemonin with sodium amalgam and acetic acid in boiling alcohol or from dihydroanemonin by the same method, and from its resemblance to α-angelica lactone and dihydroanemonin the annexed formula is assigned to it. By heating anemonin dihydrobromide, $C_{10}H_8O_4,2HBr$, m. p. 182°, with anhydrous sodium acetate in glacial acetic acid solution on the water-bath, anemonin itself is reproduced, the tetramethylene ring is therefore preserved in the derived substance. By reducing furan-2 : 5-dipropionic acid with hydrogen in the presence of platinum black, sebacic acid is produced together with a small quantity of a substance crystallising in prisms, m. p. 113°, probably *tetrahydrofuran-2 : 5-dipropionic acid*. Dihydroanemonin condenses with benzaldehyde and furfuraldehyde, producing *dibenzylidenedihydroanemonin*, colourless scales, m. p. 225°, and *difurfurylidenedihydroanemonin*, dark yellow scales, m. p. 222° respectively. *Anisylidenetetrahydroanemonic acid*, yellow scales, m. p. 160°, is produced by adding anisaldehyde to an alkaline solution of tetrahydroanemonic acid.
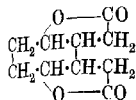
K. K.

Tannins and Similar Substances. VIII. The Tannin of the Edible Chestnut. KARL FREUDENBERG and HANS WALPUSKI (*Ber.*, 1921, **54**, [*B*], 1695—1700; cf. this vol., i, 576).—The isolation of the crude tannin from the wood is described in detail, the total yield being more than 5% of the initial material. The composite nature of the product is deduced from the fact that hydrolysis with dilute sulphuric acid gives a little quercetin, traces of gallic acid, 2% of sugar (chiefly dextrose), and 15—20% of ellagic acid, all of which are present in the combined form; simultaneously, however, the tannin is itself extensively decomposed. The action of emulsin does not lead to the separation of dextrose or of ellagic acid; the latter therefore does not appear to be present in the form of a glucoside and this hypothesis is confirmed further by the stability of its compound towards cold dilute alkali. On the other hand, Aspergillus-tannase caused a slow separation of ellagic acid when used in relatively large amount and finally gives a product from which dilute sulphuric acid does not liberate more than 3% of the acid; simultaneously, the quercetin component is hydrolysed, whilst traces of gallic acid and small amounts of sugar, chiefly dextrose, are obtained. The purified tannin is a yellowish-red substance which forms more than half of the original crude product. It shows the usual tannin reactions. It gives a blue coloration with iron salts, but does not yield a precipitate with bromine water. It is not further affected by tannase, and is not decomposed into

simpler constituents by other hydrolysing agents. It does not appear to belong to the class of ester tannins or of catechins, since it does not contain phloroglucinol, is strongly acidic, and almost insoluble in ethyl acetate. The acidity indicates a molecular weight of about 400 or some multiple thereof.

Chestnut tannin appears, therefore, to be a representative of a new type of tannin and to be very closely allied to that of the native oak (Freudenberg, *Naturwiss.*, 1920, **8**, 905), with regard to which the investigation is to be pursued.   H. W.

Syntheses in the Bergapten Group and of Other Hydroxycoumarone Derivatives. P. KARRER, A. RÜDLINGER, A. GLATTFELDER, and L. WAITZ (*Helv. Chim. Acta*, 1921, **4**, 718–728).—Since the failure to obtain a coumarin derivative, from 5-hydroxy-2-methylcoumarone-4-acrylic acid (A., 1920, i, 627) might possibly have been due to the situation of the unsaturated side chain in the 3- instead of the 4- position, 5-hydroxy-4-aldehydo-2 : 3-dimethylcoumarone has been synthesised from orcinol, and found also not to furnish a coumarin derivative. The formula for bergapten (Thoms, A., 1912, i, 40) therefore loses in probability.

5-*Hydroxy*-2 : 3-*dimethylcoumarilic acid*, $C_{11}H_{10}O_4$, m. p. 215–220°, from the ester (Kostanecki and Tambor, A., 1909, i, 319), is converted by distillation into 5-*hydroxy*-2 : 3-*dimethylcoumarone*, $OH \cdot C_6 H_2 Me {<}^{CMe}_{O}{>}CH$, m. p. 102°, from which the 4-*aldehydo*-deriv-ative, $C_{11}H_{10}O_3$, needles, m. p. 210°, is prepared by treatment with hydrocyanic acid and zinc chloride. *Aldehydophloroglucinol monomethyl ether*, $C_8H_8O_4$, of uncertain orientation, from phloroglucinol monomethyl ether, yields 7-(or 5-)*acetoxy*-5-(or -7-)*methoxy-coumarin*, $OAc \cdot C_6 H_2 (OMe) {<}^{CH}_{O}{-}^{CH}_{CO}{>}$, leaflets, m. p. 136—137°, of which the nucleus is attacked when the attempt is made to prepare the dibromide. 5-*Hydroxy*-4'-*methoxy*-2-*methyldepsenone*,

$MeO{<}\ {>}{-}CO{-}{<}\ {>}^{CMe}_{HO \quad CH}$, yellow needles, m. p. 178°, from
$\qquad\qquad\qquad\qquad O$

5-hydroxy-2-methylcoumarone by the Hoesch reaction, is reduced to 5-*hydroxy*-4'-*methoxy*-2-*methyldepsenol*, $C_{17}H_{16}O_4$, m. p. 117°. The syntheses of 5 : 4' *dihydroxy*-2-*methyldepsenone*, $C_{16}H_{12}O_4$, yellow needles, m. p. 298°, and of 5 : 3' : 4'-*trihydroxy*-2-*methyl-depsenone*, $C_{16}H_{12}O_5$, m. p. 250°, by the Hoesch reaction must be carried out at 80—90°. 5 : 4'-*Dihydroxy*-2-*methyldepsenol*, $C_{16}H_{14}O_4$, is readily oxidised by the air.   J. K.

A New Type of Iodine Compound. JOHN NORMAN COLLIE and AMY ADA BEATRICE REILLY (T., 1921, **119**, 1550—1554).

The Structural Relation of *iso*Quinoline- and Phenanthrene-Alkaloids. INGO W. D. HACKH (*Chem. News*, 1921, **123**, 178–179).—The use of structure symbols (A., 1919, i, 245) reveals an interesting structural relationship amongst alkaloids containing

the *iso*quinoline nucleus. Alkaloids such as morphine, berberine, papaverine, glaucine, narcotine, corydaline, dicentrine, protopine, cryptopine, etc., appear to belong to different groups when the usual structural formulæ are used, but when these structural formulæ, or the corresponding structure symbols, are turned so that the *iso*quinoline nucleus occupies the same relative position in each, a structural relationship, which genetically connects all these alkaloids, may be traced, and the alkaloids may be classified, thus :
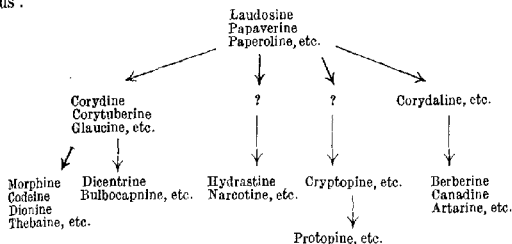
On this basis, Pschorr's formula for morphine is regarded as more probable than the formula of Freund and others.   F. M. R.

Chelerythrine. P. KARRER (*Helv. Chim. Acta*, 1921, **4**, 703—706).—Replying to criticisms by Gadamer (A., 1920, i, 872), the author claims to have been the first to point out the analogy of chelerythrine with cotarnine (A., 1917, i, 349), and maintains his view that the basic properties are due, not to the nitrogen atom, but to another group, possibly the carbonyl group. The composition of methylchelalbine, $C_{17}H_{15}O_3N$, m. p. 204°, and the melting points of chelerythrine cyanide (248—249°) and phenylhydrazone (158—160°) are confirmed, but dihydrochelerythrine is now found to melt at 162—163°.   J. K.

Reduction of Coralyne to Dihydrocoralyne and α-Coralydine. WILHELM SCHNEIDER and OTTO BÖGER (*Ber.*, 1921, **54**, [B], 2021—2031).—It has been shown previously (Schneider and Schroeter, A., 1920, i, 760) that coralyne, obtained by the action of acetic anhydride in the presence of sulphoacetic acid on papaverine, is a hexadehydrocoralydine. It is therefore to be expected that it would be reduced to coralydine, and this is shown to be the case, the α-modification of the base (cf. Pictet, A., 1913, i, 1224) being produced. Hydrogenation is, however, never complete, and dihydrocoralyne is always formed to a greater or less extent; since the base itself is
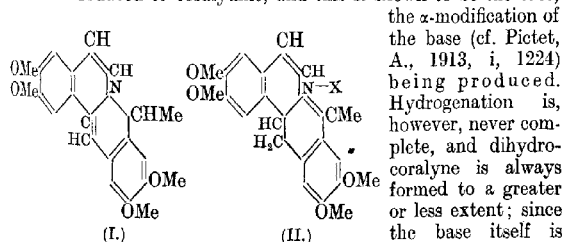
(I.)   (II.)

*g g**

intensely yellow whereas the salts are colourless, the annexed formulæ I and II are proposed for these compounds.

Coralyne sulphoacetate, $C_{22}H_{22}O_4N\cdot SO_3\cdot CH_2\cdot CO_2H,H_2O$, is reduced by zinc and sulphuric acid in boiling glacial acetic acid solution to a mixture of α-coralydine and dihydrocoralyne, the relative proportions of which depend largely on the type of zinc used; the mixed bases are converted into their iodides and subsequently, for purposes of separation, into the chlorides. The following salts of α-coralydine are described, the melting points as recorded by Pictet (*loc. cit.*) being enclosed within brackets: hydrochloride, colourless, slender rods, m. p. 255° (254°); *hydriodide*, minute, pointed needles, m. p. 242—243°; nitrate, m. p. 240—245° after incipient decomposition at about 150° (242°); platinichloride, a yellow powder, decomp. 230° (246—247°); aurichloride, a red, crystalline powder, m. p. 139° (154°); picrate, large, yellow needles, m. p. 139—140° (134°). α-Coralydine has m. p. 148°, in agreement with Pictet's observations, and is converted by iodine and alcohol into dehydrocoralydine iodide, m. p. 264·5° (264°). It is remarkable that β-coralydine does not appear to be formed.

Dihydrocoralyne, slender, yellow needles, m. p. 200°, is obtained by the rapid crystallisation from alcohol of the base, precipitated from its salts by ammonia; the moist base is extremely sensitive to atmospheric oxidation, by which it is converted into a *substance*, red needles, m. p. 241°, which has not yet been investigated completely. When boiled with water free from carbon dioxide, the *iso*-base is partly transformed into the ammonium hydroxide base, but slowly reverts to its original form when the solution is cooled. It is converted by iodine and alcohol into coralyne iodide, m. p. 278°. The following salts are described; *chloride* ($+6H_2O$), pale yellow, silky, crystalline aggregates, m. p. about 95° after softening at 85°, anhydrous, m. p. 194°; *iodide*, almost colourless, prismatic rods, m. p. 234°; *hydrogen sulphate* ($+H_2O$), m. p. 277°; *nitrate* ($+$aq), m. p. above 85°; *platinichloride*, a yellow powder, decomp. 263° after blackening above 150°; *aurichloride*, m. p. 110—115° (decomp.), and after re-solidification, decomp. above 260° after darkening at about 170°; *picrate*, m. p. about 237°.

H. W.

Harmine and Harmaline. V. The Synthesis of Norharman.
WILLIAM OGILVY KERMACK, WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON (T., 1921, **119**, 1602—1642).

The Alkaloids of the Lobelia Plant. I. HEINRICH WIELAND
(*Ber.*, 1921, **54**, [B], 1784—1788).—The isolation of two crystalline alkaloids, lobeline and lobelidine, from *Lobelia inflata* of North America is described. The former, $C_{23}H_{29}O_2N$, is a colourless, crystalline, monacid base which yields neutral salts. It does not appear to contain a ketonic or hydroxy-group and its stability towards alkali indicates the absence of the lactone group. A methoxyl radicle is not present. The nitrogen atom appears to be tertiary. Its most remarkable characteristic is the readiness

with which it yields acetophenone when warmed with water, but the fate of the remainder of the molecule has not yet been elucidated.

The isolation of lobeline from the crude mixture of bases depends on the observation that its hydrochloride can be removed from aqueous solution by repeated agitation of the latter with chloroform; the final purification is effected by crystallisation from benzene, alcohol, or ether. *Lobeline* crystallises in broad, colourless needles, m. p. 130—131°, $[\alpha]_D^{15} -42 \cdot 85°$, in alcoholic solution. The *sulphate, nitrate, bromide,* and *chloride* are placed in order of increasing solubility in water; the *platinichloride* and *mercuric chloride* compound are amorphous.

Lobelidine, $C_{20}H_{25}O_2N$, small, irregular prisms, m. p. 106°, is isolated from the final ethereal mother-liquors obtained during the preparation of lobeline. Its *hydrochloride,* matted needles, has m. p. 165° after darkening at about 160°.   H. W.

Acetyl-*N*-methyl*iso*papaverine. WILHELM SCHNEIDER and ARNOLD KÖHLER (*Ber.*, 1921, 54, [*B*], 2031—2033).—The conception of ψ-coralyne as a derivative of papaverine (cf. Schneider and Schroeter, A., 1920, i, 760) is confirmed further by the observation that its methiodide is converted by treatment with alkali into *acetyl*-N-*methyl*iso*papaverine,* yellow needles, m. p. 191° (*phenylhydrazone,* long, slender needles, m. p. 236·5°), which is readily reconverted by hydriodic acid into the original methiodide; the *iso*-base shows little tendency to pass into the ammonium form. Attempts to isolate an intermediately formed red, crystalline product (which is possibly analogous with the pyranhydrones of Schneider and Meyer, this vol., i, 680) were unsuccessful. H. W.

Preparation of a **Derivative of Thebaine.** EDMUND SPEYER, ELSE FREUND, WALTER FREUND, HELMUTH FREUND, and LISELOTTE FREUND (D.R.P. 338147; from *Chem. Zentr.*, 1921, iv, 422).—Thebaine in aqueous-alcoholic solution is treated with excess of molecular hydrogen, using colloidal metallic catalysts of the platinum group. For example, to a cooled solution of thebaine in 96% ethyl alcohol equal quantities of water and a palladium sol (1 c.c. = 0·0025 gram of Pd) are added, and the mixture is shaken in an atmosphere of hydrogen until no further absorption takes place. The palladium is then precipitated and the ethyl alcohol distilled off. After addition of aqueous ammonia, the residue is extracted with chloroform. The oil remaining after evaporation of the chloroform solution is triturated with ethyl alcohol and a *hydrochloride,* $C_{18}H_{23}O_3N,HCl$, prepared by the action of hydrochloric acid in alcoholic solution; it forms crystals, m. p. 310° (decomp.). The free *base,* $C_{18}H_{23}O_3N$, crystallises in leaflets (from alcohol) and has m. p. 145—150°. It is precipitated from solutions of its salts by excess of sodium carbonate or ammonia. With excess of alkali the precipitate of the base is redissolved; it is thus amphoteric in character. In these properties and in its stability in the presence of mineral acids, the compound described differs from tetrahydrothebaine, $C_{19}H_{25}O_3N$ (Oldenberg, A., 1913, i, 1093; Braun, A.,

1914, i, 1138). It contains one methoxyl group and has the characters of a ketone.   G. W. R.

The Free Ammonium Radicle. I. Benzoylpyridinium.
ERNST WEITZ, ADOLF ROTH, and ANNEMARIE NELKEN (*Annalen*, 1921, **425**, 161—186).—When zinc dust acts on a mixture of benzoyl chloride and pyridine the product, brown leaflets, m. p. 229° (decomp.), has the composition $C_{12}H_{10}ON=C_5H_5NBz$, and must therefore be represented by a formula containing either tervalent carbon or quadrivalent nitrogen. The formula I is regarded as most probable, but the substance is considered capable of reacting in the forms of its " valency-isomerides " II and III. It is termed *1-benzoylpyridinium*.

CH	CH	H\C
HC⟋ ⟍CH	HC⟋ ⟍CH	HC⟋ ⟍CH
HC⟍ ⟋CH	HC⟍ ⟋C⟍H	HC⟍ ⟋CH
N	N	N
Ph·CO⟋	Ph·CO	Ph·CO
(I.)	(II.)	(III.)
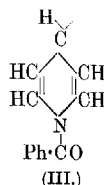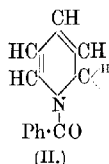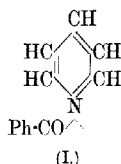
It has the normal molecular weight in boiling ethylene dibromide and in boiling chlorobenzene, but is associated in naphthalene at the freezing point.

When solutions of 1-benzoylpyridinium are shaken with air they are decolorised, half an atomic proportion of oxygen being absorbed. If they are titrated with halogens until colourless, one atom of halogen is taken up. In each case the principal products are benzoic acid and 4 : 4'-dipyridyl, the formation of which is most easily explicable on the assumption that the valency isomeride (III) takes part in the reaction. 1-Benzoylpyridinium is not a base.

4 : 4'-*Dipyridyl monobenzoate* crystallises in leaflets, m. p. 108°, and the *dibenzoate* in leaflets, m. p. 116°.   C. K. I.

The Free Ammonium Radicle. II. Benzylpyridinium.
ERNST WEITZ and ANNEMARIE NELKEN [with R. LUDWIG] (*Annalen*, 1921, **425**, 187—207; cf. preceding abstract).—1 : 1'-Dibenzyltetra-hydro-4 : 4'-dipyridyl, which was obtained by Hofmann (A., 1881, 921) and reinvestigated by Emmert (A., 1919, i, 455), has been shown by the latter (A., 1920, i, 331) to undergo dissociation in solution, forming a coloured C_{12}-compound, which may be called 1-*benzyl-pyridinium*, and has now been isolated in the crystalline condition. It forms deep red crystals, m. p. 140° (approx.), which give deep blue solutions in methyl and ethyl alcohols. The solid substance is extremely unstable and it was not found possible to make a deter-mination of its molecular weight.

Halogens react with 1-benzylpyridinium with the formation of 1-benzylpyridinium salts. The salt $(C_{12}H_{12}N)_3[CO(NO_2)_6]$ forms leaflets, m. p. 123° (decomp.).

1 : 1'-Dibenzyltetrahydro-4 : 4'-dipyridyl has the correct molecular

weight in boiling acetone, but shows indications of dissociation in benzene.   C. K. I.

Preparation of certain Alkyloxyquinolines and of their Tetrahydro-derivatives. ADOLF SONN and FRITZ BENIRSCHKE (*Ber.*, 1921, **54**, [*B*], 1730—1738).—6-Ethoxyquinoline is most advantageously prepared (yield 53%) by cautiously heating a mixture of *p*-phenetidine, glycerol, concentrated sulphuric acid, and nitrobenzene (hydrochloride [+2H$_2$O], m. p. 224°). It is reduced by tin and concentrated hydrochloric acid to 6-*ethoxy*-1 : 2 : 3 : 4-*tetrahydroquinoline*, a greenish-yellow liquid, b. p. 164—166°/17 mm., (*hydrochloride*, coarse prisms, m. p. 218°). The latter reacts with potassium cyanate to yield 6-*ethoxytetrahydroquinoline*-1-*carboxylamide*, OEt·C$_9$H$_9$N·CO·NH$_2$, colourless, lustrous plates, m. p. 154—155° after previous softening.

6 : 7-*Methylenedioxyquinoline*, pale yellow crystals which gradually become brown when preserved in a vacuum, m. p. 77°, b. p. 180—182°/22 mm. [*hydrochloride*, brown needles, m. p. 273° (decomp.)], is obtained in small yield by the action of glycerol, sulphuric acid, and nitrobenzene on 4-aminocatechol methylene ether (improved methods for the preparation of the latter and of catechol methylene ether are described).

6-Aminopiperonal (the preparation of which is described in detail, *cf.* Rilliet and Kreitmann, A., 1913, i, 1355) condenses with acetaldehyde in the presence of dilute aqueous alcoholic sodium hydroxide solution to yield a *substance*, probably

CH$_2$O$_2$:C$_6$H$_2$(NH$_2$)·CH(OH)·CH$_2$·CH:N·C$_6$H$_2$(CHO):O$_2$CH$_2$,
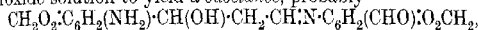
intensely yellow needles, m. p. 177°.

6 : 7-*Ethylenedioxyquinolines*, coarse crystals, m. p. 97°, b. p. 196°/18 mm. (*hydrochloride*, slender, yellow needles, m. p. 223°), is prepared in 62% yield from 4-aminocatechol ethylene ether, nitrobenzene, sulphuric acid, and glycerol. It is reduced by tin and hydrochloric acid to 6 : 7-*ethylenedioxy*-1 : 2 : 3 : 4-*tetrahydroquinoline*, needles, m. p. about 78° (*hydrochloride*, slender, lustrous needles, m. p. 201°), b. p. 207°/20 mm.   H. W.

Manufacture of Symmetrical Alkylated *m*-Phenylenediamines. BRITISH DYESTUFFS CORPORATION, LTD., ARTHUR GEORGE GREEN, and ARTHUR BRITTAIN (Brit. Pat. 168689).—Symmetrically alkylated *m*-phenylenediamines are obtained by the action at high temperatures of primary or secondary alkylamines or their salts on resorcinol in aqueous or alcoholic solution, and separation of the alkylated phenylenediamine produced from any unchanged resorcinol and from aminophenolic substances. The presence of sulphurous acid is advantageous to the reaction, and hence the alkylamine sulphites can conveniently be employed. For example, a 67% yield of *m*-phenylenedimethyldiamine is obtained by heating in an autoclave for twelve hours at 125° 55 parts of resorcinol, 66 parts of 35% solution of methylamine sulphite, and 125 parts of 25% aqueous solution of methylamine. The product is separated from unchanged methylamine and resorcinol and from *m*-methylaminophenol by the usual methods, and is finally purified by distillation in a vacuum; it has b. p. 170°/10 mm.   G. F. M.

Catalysis.   I.   Reduction of Uracil to Hydrouracil. TREAT
B. JOHNSON and ELMER B. BROWN (*Proc. Nat. Acad. Sci.*, 1921, 7,
75—77).—The authors have shown that uracil may be quantitatively
converted into hydrouracil in the presence of colloidal platinum by
gaseous hydrogen.   The catalyst is prepared by adding a 10%
solution of chloroplatinic acid to a solution of gum arabic and
reducing to the metal by gaseous hydrogen.· An aqueous solution
of uracil is mixed with the catalyst and treated with gaseous
hydrogen at a pressure of two atmospheres and at temperature
75—85°.   The product is pure hydrouracil, m. p. 272°.   J. F. S.

***N*-Alkyl Derivatives and *N*-Carboxylic Esters of Indazole.**
K. VON AUWERS and W. SCHAICH (*Ber.*, 1921, **54**, [*B*], 1738—
1770; cf. A., 1919, i, 455; 1920, i, 638, 640).—Stereoisomerism
has only been observed previously among *N*-acyl derivatives of
indazole and not with the alkyl compounds of which the methyl and
ethyl derivatives alone have been examined.   Since in the former
cases the occurrence of the phenomenon appeared to depend, in
part, at any rate, on the magnitude of the acyl group, the benzyl-
indazoles have now been examined.   In this case, also, stereoiso-
merism is not observed, but the results are otherwise surprising.
The product obtained by the action of benzyl iodide on silver
indazole is not identical with the 2-benzylindazole described by
Fischer and Blochmann (A., 1902, i, 645), and is identified as
1-benzylindazole.   Fischer's compound is obtained by the action
of benzyl chloride on indazole at 100°, but in a lengthy series of
experiments 1-benzylindazole was prepared uniformly from the
same substances at 140—180°, whereas in a second series, carried
out under apparently precisely similar conditions, the 2-benzyl
derivative was uniformly produced.   The reason of this apparent
anomaly has not been elucidated, but it is definitely shown that
each substance is a primary product and that interconversion does
not occur under the experimental conditions adopted.
    The unexpected results obtained during the preparation of benzyl-
indazole has led to a re-examination of the alkylation of the parent
substance by a considerable number of alkyl haloids.   It is found
that the two isomerides are produced from indazole and alkyl
haloid in the presence of boiling alcoholic alkali hydroxide, the
proportions being in general about equal; with allyl bromide the
1-derivative predominate⸱ to a marked degree, whilst *iso*propyl
bromide gives the 1-isomeride exclusively.   Indazole and alkyl
haloids at 100° yield the 2-derivatives as sole products, except in
the case of *iso*propyl bromide, with which reaction does not take
place.   Methyl, allyl, and benzyl iodides are the only haloids
which react with an ethereal suspension of silver indazole with
sufficient rapidity at the ordinary temperature;   the former gives
exclusively 2-methylindazole under these conditions, thus con-
firming earlier observations, whereas the two latter yield only
the corresponding 1-compounds.   With ethyl iodide, it is found
that increase in temperature very greatly favours the production
of the 1-isomeride, and the same phenomenon is also observed in

a less degree with methyl iodide. The boiling points of the 2-derivatives are uniformly about 25° higher than those of the 1-isomeride, the melting points of the picrates are similarly higher, but the differences exhibited are here irregular.

Indazole-2-carboxylic esters are prepared by boiling indazole with alkyl chloroformates or by the action of the latter on silver indazole at the atmospheric temperature. The methods lead to the production of identical substances in each case, and instances of stereoisomerism as with 2-acetyl-, 2-propionyl-, and 2-benzoyl-indazoles are not observed. The corresponding free acids are exceedingly unstable and readily decompose, even at 0°, into indazole and carbon dioxide. The esters exhibit the remarkable property of eliminating carbon dioxide with greater or less readiness when heated, passing generally into the corresponding alkylindazoles.

The theory of the reactions is discussed at length, and with particular reference to the action of alkyl haloids on silver indazole. The most probable hypothesis appears to be that the two components form initially a loose additive product from which silver haloid is eliminated, leaving for the moment the indazyl and alkyl radicles with free valencies. The former then undergoes isomerisation to an equilibrium mixture in accordance with the

scheme $C_6H_4{<}^{CH}_{N--}{>}N-\left[\rightarrow C_6H_4{<}^{CH}_{N--}{>}N-\right]\rightarrow C_6H_4{<}^{CH}_{-N}{>}N,$

and the subsequent addition of the alkyl group to the 1- or 2-nitrogen atom then depends on the distribution of the free valency in the indazyl radicle and the affinity demand of the alkyl group.

The following individual compounds are described : 1-*Benzyl-indazole*, colourless, lustrous needles, m. p. 64·5° (*picrate*, coarse, yellow crystals, m. p. 89·5—90·5°). 2-*Benzylindazole-3-carboxylic acid*, almost colourless needles, m. p. 194°, which gives 2-benzyl-indazole, m. p. 67—69° (picrate, m. p. 160—162°) when distilled. 1-*Benzylindazole-3-carboxylic acid*, small, colourless needles, m. p. 164·5—165·5°, which when heated is converted into 1-benzylindazole.

1-*Benzyl-2-methylindazolium iodide*, $C_6H_4{<}^{CH----}_{N(C_7H_7)}{>}N{<}^{Me}_I$, needles or coarse prisms, m. p. 175° (corresponding *picrate*, m. p. 139°), which decomposes when heated in a vacuum into a mixture of 2-methylindazole and 1-benzylindazole. 2-*Benzyl-1-methylindazolium iodide*, $C_6H_4{<}^{CH}_{NMe}{>}N{<}^{C_7H_7}_I$, slender, colourless needles, m. p. 148—149° (corresponding *picrate*, m. p. 195—196°, decomp.), which decomposes into 1-methylindazole when heated in a vacuum (2-benzylindazole when treated with an excess of methyl iodide yields 1 : 2-dimethylindazolium iodide). 1 : 2-*Dimethylindazolium hydroxide*, an almost colourless, crystalline mass which absorbs carbon dioxide readily from the air and yields 1-methylindazole when distilled. 1-*Propylindazole*, a colourless liquid, b. p. 118—119°/10 mm. (*picrate*, yellow needles, m. p. 99—100°). 2-*Propyl-indazole*, a colourless liquid, b. p. 157°/20 mm. (*picrate*, m. p. 151—152°). 1-iso*Propylindazole*, a colourless liquid, b. p. 117—118°/

12 mm. (*picrate*, yellow needles, m. p. 120°). 1-iso*Amylindazole*, a colourless liquid, b. p. 154—155°/17 mm. [*picrate* (?) m. p. 63—65°]. 2-iso*Amylindazole*, a colourless liquid, b. p. 178—179° 17 mm. (*picrate*, yellow, matted needles, m. p. 115—116°). 1-*Allyl-indazole*, a colourless liquid, b. p. 126°/12 mm. (*picrate*, slender, yellow needles, m. p. 112·5—113·5°). 2-*Allylindazole*, a colourless liquid, b. p. 144—145°/12 mm. (*picrate*, yellow needles, m. p. 125—126°). *Ethyl indazole-2-carboxylate*, a colourless liquid, b. p. 156°/10 mm. [additive *product* with mercuric chloride, m. p. (indefinite) 115—123°; a picrate is not formed], which decomposes when distilled under diminished pressure into a mixture of 1- and 2-ethylindazoles and is converted by methyl iodide at 100° into 1 : 2-dimethylindazolium iodide. *Methyl indazole-2-carboxyl-ate*, long needles, m. p. 59—60°, b. p. 152—153°/15 mm., which gives much resinous matter and 2-methylindazole when distilled. iso*Amyl indazole-2-carboxylate*, a viscous liquid, b. p. 187·5°/11·5 mm., which, when heated, yields *iso*amyl alcohol, indazole, and 2-*iso*amylindazole. *Benzyl indazole-2-carboxylate*, colourless needles, m. p. 83—84°, which readily yields a mixture of the 1- and 2-benzyl-indazoles. *Phenyl indazole-2-carboxylate*, colourless, lustrous needles, m. p. 91°, b. p. 215°/11 mm., which yields mainly resinous matter in addition to phenol and indazole when heated at the atmospheric pressure for a considerable time.   H. W.

dl-β-2-**Furyl**-α-**alanine.** TAKAOKI SASAKI (*Ber.*, 1921, **54**, [B], 2056—2059).—The preparation of the substance is effected according to the author's glycine anhydride method (this vol., i, 196).

2 : 5-*Diketo*-3 : 6-*difurfurylidinepiperazine*,

$$C_4H_3O\cdot CH\text{:}C{<}^{CO\cdot NH}_{NH\cdot CO}{>}C\text{:}CH\cdot C_4H_3O,$$
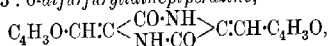
yellow needles, m. p. 289—290° (corr., decomp.), is obtained in 83·7% yield by the action of glycine anhydride on freshly-distilled furfuraldehyde in the presence of acetic anhydride and anhydrous sodium acetate at 120—130°. It is reduced by sodium and alcohol (95%) to 2 : 5-*diketo*-3 : 6-*difurfurylpiperazine*, m. p. 216° (corr.), which is hydrolysed by boiling aqueous barium hydroxide solution to dl-β-2-*furyl*-α-*alanine*, $C_4H_3O\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, m. p. 260° (corr.); the latter is converted by phenylcarbimide into α-*phenylcarbamido*-β-2-*furylpropionic acid*,

$$C_4H_3O\cdot CH_2\cdot CH(NH\cdot CO\cdot NHPh)\cdot CO_2H,$$

m. p. 162—163° (corr.), and by naphthalene-β-sulphonyl chloride into N-*naphthalenesulphonyl*-β-2-*furyl*-α-*alanine*,

$$C_4H_3O\cdot CH_2\cdot CH(NH\cdot SO_2\cdot C_{10}H_7)\cdot CO_2H,$$

decomp. 222° after darkening at 208°.   H. W.

o-**Chlorodinitrotoluenes. III. Bases derived from 2-Chloro-4 : 5-dinitrotoluene.** GILBERT T. MORGAN and WILLIAM ARTHUR PERCIVAL CHALLENOR (T., 1921, **119**, 1537—1546).

o-**Quinones and 1 : 2-Diketones. III. Constitution of Phenanthraquinoneimide Anhydride.** A. SCHÖNBERG and BERTA ROSENTHAL (*Ber.*, 1921, **54**, [B], 1789—1802).—The elucida-

tion of the constitution of acenaphthaquinoneimide anhydride (this vol., i, 275) has induced the authors to investigate phenanthraquinoneimide anhydride. The latter is found to lose its oxygen when heated and to yield a compound, $C_{28}H_{16}N_2$, which is not

identical with the azine, $C_{12}H_8 \begin{array}{c} N \\ C \quad C \\ \big< \| \quad \| \big> \\ C \quad C \\ N \end{array} C_{12}H_8$. Further, it

combines readily in molecular proportions with water, alcohols, acetic acid, and hydrogen chloride, giving products from which the original material is readily regenerated. The latter properties point to the presence of the ethylene oxide ring. The annexed formulæ (I and II) are therefore proposed

(I.)   (II.)
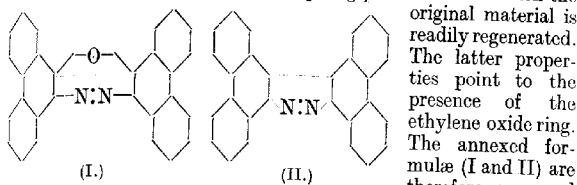
for the imide anhydride and the corresponding oxygen-free compound.

Phenanthraquinoneimide hydrochloride is obtained in the form of extremely unstable, red needles when a dry ethereal solution of hydrogen chloride is slowly added to the imide dissolved in a well-cooled mixture of ether and chloroform. The corresponding *picrate* crystallises in dark red needles, m. p. above 150° (decomp.). Phenanthraquinoneimide anhydride, prepared by short treatment of the imide with boiling acetic anhydride, forms pale yellow needles, m. p. 252° (*picrate*, short, scarlet needles, m. p. 216—217°); it can also be prepared by heating the imide. It is oxidised by chromic acid in glacial acetic acid solution to phenanthraquinone. When heated above 380° it is partly carbonised and gives a sublimate (about 70%) of *diphenanthrapyridazine* (formula II), yellow needles, m. p. 290°, which is converted by chromic acid into phenanthraquinone; it is stable towards boiling alkaline permanganate and is not reduced by zinc dust in acetic acid solution. It yields a *picrolonate* and a *picrate*, yellow needles, m. p. 255—256° after previous softening.

The imide anhydride is readily hydrolysed by solutions of alkali to cis-4 : 5-*dihydroxydiphenanthrapyridazine*-4 : 5-*dihydride*,

$C_{12}H_8 \begin{array}{c} OH \quad HO \\ \big\langle =N\text{-}N= \big\rangle \end{array} C_{12}H_8$, colourless prisms ($+$EtOH), decomp. 305°
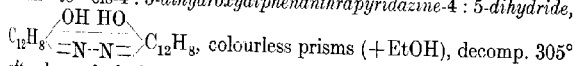
after loss of alcohol at about 220°, which is readily reconverted into the imide anhydride by treatment with benzoyl chloride according to Schotten-Baumann, by warming with acetic anhydride or by being melted. The action of acids on the imide anhydride results in the utilisation of one molecule for the rupture of the ethylene oxide ring and of a second molecule in the formation of a salt with the basic compound thus formed; the elimination of the second molecule and liberation of the base without affecting the first molecule is a matter of considerable difficulty. The *acetate,*

$C_{12}H_8\!\!\underset{=N-N=}{\overset{OAc\ HO}{\diagup\diagdown}}\!\!C_{12}H_8$, colourless prisms, is formed from the imide anhydride and boiling glacial acetic acid, and is converted by boiling nitrobenzene into the free *base*, colourless prisms, m. p. 302—305° (violent decomp.); it is hydrolysed in alkaline solution to the corresponding 4 : 5-dihydroxy-compound. cis-4-*Hydroxy-5-propionoxydiphenanthrapyridazine-4 : 5-dihydride propionate* is prepared in a similar manner, and is converted above 220° into the corresponding free *base*, m. p. 306° (decomp.). The *hydrochloride* of cis-4-*chloro-5-hydroxydiphenanthrapyridazine-4 : 5-dihydride* is obtained from the imide anhydride and hydrogen chloride in warm chloroform, but the isolation of the corresponding base could not be accomplished satisfactorily. Treatment of the imide anhydride with a boiling solution of sulphuric acid in methyl alcohol leads to the formation of cis-4-*hydroxy-5-methoxydiphenanthrapyridazine-4 : 5-dihydride*, colourless prisms (+MeOH), m. p. 202°; the corresponding *picrate*, yellow prisms, m. p. 231°, after slight previous softening, and *sulphate*, colourless needles, are described. cis-4-*Hydroxy-5-ethoxydiphenanthrapyridazine-4 : 5-dihydride* crystallises in colourless prisms, m. p. 180° [the *nitrate*, colourless, rhombic prisms, decomp. 174°, *chloride*, m. p. 227—228° (decomp.) after previous softening, and *picrate*, yellow prisms, m. p. 230°, are described]. cis-4-*Hydroxy-5-n-propoxydiphenanthrapyridazine-4 : 5-dihydride* forms colourless prisms, m. p. 149°.

H. W.

Indigotin. W. MADELUNG (*Zeitsch. angew. Chem.*, 1921, **34**, 482—483, 486—488).—The question as to how far Baeyer's formula for indigotin is in agreement with the chemical behaviour and physical properties of indigotin, and known facts with regard to the relation between colour and chemical constitution, is critically discussed. It is concluded that the facts are interpreted more correctly by one of the following formulæ :

$$C_6H_4\diagdown\overset{\diagup O\diagdown\ \ H}{\underset{\diagdown N\diagup}{\underset{\diagup\ \ \ \diagdown}{C=C}}}\overset{N}{\underset{C}{\diagdown}}\diagup C_6H_4 \qquad C_6H_4\diagdown\overset{\diagup O\diagdown\ \ H}{\underset{\diagdown N\diagup}{\underset{\diagup\ \ \ \diagdown}{C=C}}}\overset{N}{\underset{C}{\diagdown}}\diagup C_6H_4$$

(I.)   (II.)
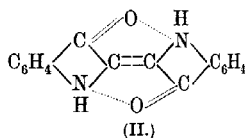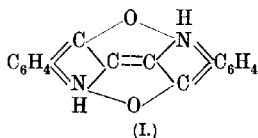
The choice between I, which is more nearly related to the conceptions of Claasz, and II, which is more in agreement with the conceptions of Lifschitz and Lourié, is regarded as unimportant, the point of real importance in the proposed formulæ being that the carbonyl and imino-groups are at each end of a five-membered conjugated system, thus $O\!=\!C\!-\!C\!=\!C\!-\!NH$. Such an arrangement is to be found in other vat dyes of both the indigoid and anthracene series, and the stability and technical utility of these dyes are attributed to this atomic grouping, which is as important in this series as is the proximity of the carbonyl and hydroxyl groups in the dyes of the alizarin series, where the chain $O\!=\!C\!-\!C\!=\!C\!-\!OH$ plays a

similar rôle. If the above formulæ are accepted, indigotin is to be regarded as a derivative of the coloured and stable modification of dibenzoylethylene.

Indigotin on treatment with acetic anhydride and zinc dust in presence of a little acetyl chloride is converted into diacetylanhydro-indigo-white,
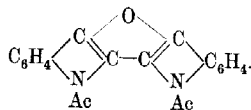
The acetyl groups cannot be removed from this compound without far-reaching decomposition. When indigotin in alcoholic hydrochloric acid suspension is reduced with iron powder, a sparingly soluble monohydrochloride of a base is obtained. This base proved to be a hydrogenated anhydroindigo-white containing the hydrofuran ring, and attempts to dehydrogenate this compound with a mild oxidising agent resulted in the formation of anhydroindigo-white, two molecules of which then condense, with elimination of water.

The addition of indigo-white to warm alcoholic hydrochloric acid, with or without the exclusion of air, results in the formation of indigotin and the hydrogenated anhydroindigo-white.   F. M. R.

Alkali Fusions.   III.   Fusion of Phenylglycine-o-carboxylic Acid for the Production of Indigotin.   MAX PHILLIPS (*J. Ind. Eng. Chem.*, 1921, **13**, 759—762; cf. A., 1920, i, 732).—The maximum yield (89%) of indigotin is obtained when 1 molecule of phenylglycine-o-carboxylic acid and 12 to 16 molecules of potassium hydroxide are fused together at 260° for ten minutes. With sodium hydroxide, the maximum yield (69%) is obtained by using 28 to 32 molecules of the alkali and fusing the mixture at 270° for twenty-five to thirty minutes.   W. P. S.

Constitution of the *iso*Isatogens.   PAUL RÜGGLI and ADOLF BOLLIGER (*Helv. Chim. Acta*, 1921, **4**, 626—637; cf. A., 1919, i, 221).—The isomerism of the isatogens with the lighter coloured products obtained from them is confirmed by molecular weight determinations of the product derived from methyl isatogenate, and the latter are termed *iso*isatogens. It is suggested that the two series are desmotropic and that the formation of isatin from o-nitrophenylpropiolic acid (Baeyer, A., 1886, 274) involves a similar change. The formula previously proposed for the new compounds is not finally adopted, although no evidence has been discovered against it. Thus, the change is not analogous to the change of nitrobenzene into *p*-nitrosophenol, since the *iso*isatogens have no phenolic properties, and methyl *iso*isatogenate is reduced by stannous chloride to methyl indoxylate, although not as readily as methyl isatogenate. Further, the *iso*-esters, either alone or, with less accompanying decomposition, in glacial acetic acid solution are converted by heat into their isomerides. The change is, however, best accomplished by heating the *iso*-compound with phenylcarbimide (cf. Beckmann,

A., 1909, i, 390; Diels and Salomon, A., 1919, i, 226; Staudinger, A., 1919, i, 584). Methyl *iso*isatogenate furnishes an oxime at the ordinary temperature which is identical with that produced from the quinonoid isomeride, and since it exhibits oxidising properties, (cf. Pfeiffer, A., 1916, i, 327) is derived from this. This exceptional observation is unexplained. *Ethyl isoisatogenate*, $C_{11}H_9O_4N$, m. p. 146°, forms yellow crystals. *Ethyl* β-*o*-*nitrophenylbromoacrylate*, $C_{11}H_{10}O_4NBr$, m. p. 59°, results from the action of pyridine on ethyl αβ-dibromo-β-*o*-nitrophenylpropionate. Di-isatogen (Baeyer, A., 1882, 619) is best obtained from *oo*-dinitrodiphenyldiacetylene by illumination of its chloroform solution.   J. K.

Action of Phenyl Hydrazine on Isatogens. PAUL RÜGGLI and ADOLF BOLLIGER (*Helv. Chim. Acta*, 1921, **4**, 637—644; cf. preceding abstract).—The action of phenylhydrazine on 6-nitro-2-phenylisatogen results in the formation of 6-*nitro-2-phenylindoxyl*, $C_{14}H_{10}O_3N_2$, orange-red leaflets, m. p. 215.° Its dilute solution in acetic anhydride in presence of sulphuric acid furnishes an α-*acetyl* derivative, $C_{16}H_{12}O_4N_2$, orange-yellow needles, m. p. 192—193°, whilst in more concentrated solution at 40° an isomeric β-*derivative*, $C_{16}H_{12}O_4N_2$, greenish-yellow needles, m. p. 172°, is produced. 6-Nitro-2-phenylindoxyl yields a *quinhydrone*, $C_{28}H_{18}O_7N_4$, brownish-black needles, m. p. 208—210°, when mixed in hot glacial acetic acid solution with 6-nitro-2-phenylisatogen, but not with its isomeride. The latter is also distinguished by its conversion by means of phenylhydrazine into 6-*nitro-3-keto-2-phenylindoleninephenylhydrazone*, $C_{20}H_{14}O_2N_4$, red needles, m. p. 260—261°. *Methyl 3-ketoindolenine-2-carboxylate*, $C_{10}H_7O_3N$, yellow needles, m. p. 255° (decomp.), (*oxime*, $C_{10}H_8O_3N_2$, yellow needles, m. p. 221°) is obtained by the action of phenylhydrazine on a cold dilute solution of methyl isatogenate, but at higher temperatures methyl indoxylate is produced, accompanied by what is probably *methyl 3-ketoindolenine-2-carboxylate-phenylhydrazone*, $C_{16}H_{13}O_2N_3$, orange crystals, m. p. 218°, when the reaction is particularly energetic. Methyl *iso*isatogenate does not react with phenylhydrazine.   J. K.

Paired Cyclamines. I. 2-(2-Quinolyl)Cyclamines; Valency Formula of Quinoline. ALEXANDER P. SMIRNOV (*Helv. Chim. Acta*, 1921, **4**, 802—811).—2-(2'-*Pyridyl*)*quinoline*,
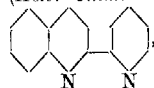
, m. p. 96° (*platinichloride*, orange-yellow needles,

m. p. 197°, decomp.; *aurichloride*, yellow needles, m. p. 211°, decomp.; *picrate*, greenish-yellow leaflets, m. p. 183°), results from the condensation of *o*-aminobenzaldehyde with 2-pyridyl

methyl ketone. 2 : 2'-*Diquinolyl*, , leaflets,

m. p. 196° (*platinichloride*, orange-yellow leaflets, m. p. above 300°;

aurichloride, unstable yellow needles; *picrate*, yellow needles, m. p. 210°), formed by condensation of *o*-aminobenzaldehyde with either 2-quinolyl methyl ketone or diacetyl. 2-(2'-*Pyrryl*)*quinoline*,
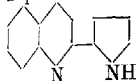
, leaflets, m. p. 129° (*platinichloride*, yellowish-

brown prisms, m. p. 210°, decomp.; *aurichloride*, yellow and unstable), prepared similarly from *o*-aminobenzaldehyde or from potassium pyrrole and 2-chloroquinoline followed by isomerisation, colours a

pine-shaving yellow. 2-(2'-*Glyoxalinyl*)*quinoline*, ,
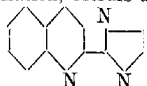
prisms, m. p. 119° [*platinichloride*, orange prisms, m. p. 330° (decomp.); *aurichloride*, golden-yellow leaflets, m. p. 205° (decomp.); *picrate*, needles, m. p. 201°], prepared from the silver salt of glyoxaline and 2-chloroquinoline.

2-(2'-Pyridyl)- and 2-(2'-quinolyl)-quinolines do not form complex ferro-compounds as do 2 : 2'-dipyridyl and *o*-phenanthroline (Blau, A., 1899, i, 387). This is attributed to internal saturation of the residual nitrogen valency in the former compounds, the differences being expressed by the formulæ (I—III), which also explain the destruction of the " benzene " nucleus by alkaline oxidation. The attack of the pyridine ring by reduction or acid oxidation is explained by assuming formulæ IV and V for the primary reduction product and the ions produced in acid solution.

(I.)   (II.)   (III.)   (IV.)   (V.)
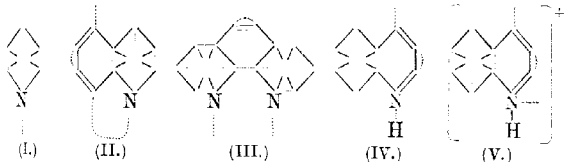
J. K.

Ring Closure with Hydrazinedicarbonamides containing Sulphur. I. Dithiourazole and Iminothiourazole. F. ARNDT and E. MILDE (*Ber.*, 1921, **54**, [*B*], 2089—2110).—The products of the internal condensation of hydrazinedithiocarbonamide and hydrazinedicarbothiophenylamide have been examined by Freund (A., 1894, i, 97; 1895, i, 400), who considered them to be derivatives of thiourazole, and later by Busch and Schmidt (A., 1913, i, 907) and by Busch and Lotz (A., 1915, i, 317), who proved them to be thiodiazoles. The internal condensation of the methyl and benzyl ethers of hydrazinedithiocarbonamide has now been investigated.

Hydrazinedithiocarbonamide is readily methylated by methyl sulphate in aqueous alkaline solution and the production of the mono- or di-methylated product is easily regulated by suitably adjusting the quantity of sodium hydroxide used. *Hydrazinedithiocarbonamide monomethyl ether*, $NH_2 \cdot CS \cdot NH \cdot NH \cdot C(SMe) \colon NH$, crys-

tallises in lustrous needles, m. p. 174°, whereas the *dimethyl* compound, $N_2H_2[C(SMe):NH]_2$, forms broad needles, m. p. 132°; the *nitrate* and *sulphate* of the latter are freely soluble in water; the *dihydrochloride* has m. p. 198°. The dimethyl compound loses methyl mercaptan at 155—200° and forms *iminomethylthiolurazole,*

$$NH{<}{\overset{\displaystyle C(:NH)\cdot NH}{\underset{\displaystyle C(SMe):N}{}}}\text{, colourless crystals, m. p. 135°, which is also}$$

formed when the compound is boiled with 2*N*-sodium hydroxide solution or when an alcoholic solution of dimethyl cyanimidodithiocarbonate, $C(SMe)_2:N\cdot C:N$, is boiled with hydrazine hydrate the corresponding *nitrate*, m. p. 157°, *mono-silver* salt and *monobenzoate,* m. p. 144—145°, are described.

Iminothiourazole, $NH{<}{\overset{\displaystyle C(:NH)\cdot NH}{\underset{\displaystyle CS\text{-----}NH}{}}}$, short, colourless needles,

m. p. 303° (decomp.), is prepared by the action of very concentrated, aqueous potassium hydroxide solution on hydrazinedithiocarbonamide, of 2*N*-sodium hydroxide solution on hydrazinedithiocarbonamide monomethyl ether or of hydrazine hydrate on thiocyanic acid. It is a powerful acid and does not exhibit any basic characteristics. Its constitution is elucidated by its conversion into iminothiourazole monomethyl ether by methyl sulphate and sodium hydroxide. With ammoniacal silver nitrate it gives a *di-silver* salt, whereas in dilute nitric acid solution a *mono-silver* compound is produced. The (?) *dibenzoyl* derivative, lustrous needles, m. p. 177°, is described. Its solution in aqueous sodium hydroxide is oxidised by potassium ferricyanide to the corresponding *disulphide,* colourless crystals, m. p. 240° (decomp.), after softening at 238° [*nitrate*, m. p. 130° (violent decomp.)]. 2 : 5-*Dimethylthiolurazole,*

$$NH{<}{\overset{\displaystyle C(SMe):N}{\underset{\displaystyle C(SMe):N}{}}}\text{, colourless needles, m. p. 91° after softening at}$$

90°, is prepared by the action of boiling aqueous 2*N*-sulphuric acid on hydrazinedithiocarbonamide dimethyl ether; the *nitrate*, long, slender needles, m. p. 95°, *silver* salt and *monobenzoate,* m. p. 95°, are described. When treated with fuming hydriodic acid it gives *methylthiolthiourazole,* almost colourless needles, m. p. 254° (decomp.) after softening at 250° (complete demethylation does not appear to occur), the constitution of which is elucidated by its ready re-conversion into the initial substance under the action of methyl sulphate and alkali hydroxide. The monomethyl compound is oxidised by potassium ferricyanide to the corresponding *disulphide,* $C_6H_8N_6S_4$, m. p. 203° after softening at 201°, the *nitrate* of which was also prepared.

Dithiourazole, $NH{<}{\overset{\displaystyle CS\cdot NH}{\underset{\displaystyle CS\cdot NH}{}}}$, almost colourless crystals, m. p.

195—196°, is obtained under certain conditions which are described fully in the original by the action of hydrazine hydrate on methyl trithioallophanate, $SMe\cdot CS\cdot NH\cdot CS\cdot NH_2$, in aqueous solution; the *silver* salts, $C_2HN_3S_2Ag_2$ and $C_2N_3S_2Ag_3$, are prepared in dilute acid and ammoniacal solutions respectively.

Hydrazinedithiocarbonamide monomethyl ether is transformed by

boiling 2N-hydrochloric acid into *methylthioliminothiodiazole*,

$S<^{C(:NH)\cdot NH}_{C(SMe):N}$, long pointed needles, m. p. 176—178° (the spar-

ingly soluble *hydrochloride* and the *silver* salt are described); the constitution of the substance is deduced from its markedly basic properties, from its production by the methylation of the thiol-iminothiodiazole of Freund (*loc. cit.*) and Busch (*loc. cit.*), and by the direct synthesis of the compound of the only alternative

formula, $NH<^{C(SH)=N}_{C(SMe):N}$, which has completely different properties.

Hydrazinedithiocarbonamide is converted by benzyl chloride in the presence of aqueous potassium hydroxide solution into the corresponding *monobenzyl ether*, short, coarse needles, m. p. 148° [which is transformed by sulphuric acid into benzylthiolimino-thiodiazole, m. p. 157° (cf. Busch, *loc. cit.*) and by sodium hydroxide into benzyl mercaptan and iminothiourazole] and the *dibenzyl ether*, lustrous leaflets, m. p. 94° (which readily yields sparingly soluble *salts* with mineral acids and is remarkably resistant towards the action of heat and of alkali). The latter is converted by 2N-sulphuric acid in aqueous alcoholic solution into 2 : 5-*dibenzyl-thiolurazole*, m. p. 111° after softening at 108°.

Hydrazinedithiocarbophenylamide is transformed by boiling 2N-sodium hydroxide solution into 2-phenylimino-5-thio-1-phenyl-urazole, m. p. 205° (cf. Busch, *loc. cit.*). It is transformed by methyl sulphate into the corresponding *dimethyl* derivative, $C_{16}H_{18}N_4S_2$, lustrous needles, m. p. 140°. The latter is converted by acids or by potassium hydroxide solution into methyl mercaptan and phenylmethylthiolphenylurazole, m. p. 226°.   H. W.

5-Hydroxyhydantoin. HEINRICH BILTZ and MARIA KOBEL (*Ber.*, 1921, **54**, [B], 1802—1828).—Several substances are described in the literature as glyoxylurea [5-hydroxyhydantoin]; of these, Strecker's and Medicus's (this Journ., 1875, 555) " crystalline gly-oxylurea " has recently been shown to be identical with allantox-aidin (Biltz and Robl, A., 1920, i, 885). The authors now in-vestigate the amorphous products.

In the preliminary part of the work, attempts to isolate glyoxyl-urea from uroxanic acid, from allantoin, and from allanturic acid according to directions given in the literature are described. It appears to be impossible, however, to isolate a pure glyoxylurea, $C_3H_4O_3N_2$, from these materials, the main difficulty consisting in the removal of allantoin; even when this has been largely elimin-ated, a pure product is not obtained and the only possibilities of success appear to lie in the selection of an original material which cannot yield allantoin or in the choice of conditions under which the latter is destroyed. The latter effect can be achieved by treatment of the crude product with nitrous fumes, or preferably successively with hot hydrochloric acid and nitrous fumes; the purified product then gives analytical data approximating to those required by the formula $C_3H_4O_3N_2$. As starting-point for the experiments in the former direction, alloxanic acid [5-hydroxy-

hydantoin-5-carboxylic acid] (Biltz, Heyn, and Bergius, A., 1917, i, 289) is chosen. An improved method of preparing this substance from alloxan is fully described, and it is shown to be decomposed by hot water into Schlieper's leucoturic acid, a second substance (see later), and difluan, $C_3H_4O_3N_2$, a white, amorphous, voluminous powder which is extremely hygroscopic; it suffers incipient decomposition at 120° and becomes brown at 180°. It is thus possible in two ways to secure preparations, $C_3H_4O_3N_2$, which are precisely similar in all their properties and constitute the main component of the "amorphous glyoxylurea" of the literature. The substance is stable towards hydrochloric acid, but is converted by concentrated sulphuric acid into oxalic acid and ammonia. It is strongly acidic, and liberates carbon dioxide from sodium carbonate. It is very sensitive to the action of alkali hydroxides, yielding oxalic acid, and carbamide or ammonia. This property renders the preparation of well-defined salts a matter of considerable difficulty, but a revision of the recorded data appears to indicate strongly that the material is a monobasic acid. It is smoothly, but under somewhat energetic conditions, oxidised by potassium dichromate and sulphuric acid to parabanic acid. It cannot be reduced by phosphorus and fuming hydriodic acid to hydantoin. Its failure to react with phenylcarbimide indicates the absence of a hydroxyl group. Since, further, the physical and chemical properties differ widely from those of 5-hydroxy-1 : 3-dimethylhydantoin (succeeding abstract), the authors are drawn to the conclusion that their product is not 5-hydroxyhydantoin, but dehydrohydantoic acid, $NH_2 \cdot CO \cdot N\colon CH \cdot CO_2H$. (It is proposed to retain the name "glyoxylurea.") This conception is confirmed by its transformation with diazomethane into *methyl* N-*methyldehydrohydantoate*,

$$NHMe \cdot CO \cdot N\colon CH \cdot CO_2Me,$$
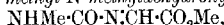
an amorphous, extremely hygroscopic powder, with benzoic anhydride into the corresponding mixed *anhydride*, $C_{10}H_8O_4N_2$, forming pale yellow, micro-crystalline needles, m. p. 252° (decomp.) after darkening at 220°, and with acetic anhydride into a *substance*, $C_5H_6O_4N_2$, an almost colourless, very hygroscopic powder. It is attacked only with difficulty by nitrous acid.

The authors' hypothesis receives considerable confirmation from the isolation of 5-hydroxyhydantoin which, although previously nearly completely overlooked, is now shown to be the main product of the decomposition of alloxanic acid by water,

$$CO\begin{smallmatrix}NH \cdot C(OH) \cdot CO_2H \\ NH \cdot CO\end{smallmatrix} \longrightarrow CO_2 + CO\begin{smallmatrix}NH \cdot CH \cdot OH \\ NH \cdot CO\end{smallmatrix}.$$
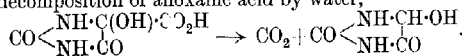
The main portion is mixed with the leucoturic acid, from which it is readily separable by taking advantage of its ready solubility in alcohol, in which the latter is insoluble. 5-Hydroxyhydantoin crystallises in needles, m. p. 165°. It is very stable towards alkali, faintly acid towards litmus, and does not liberate carbon dioxide from metallic carbonates. It is oxidised by potassium dichromate to parabanic acid, and reduced by hydriodic acid to hydantoin. It is readily converted by diazomethane into 5-*methoxy*-3-*methylhydantoin*, a yellow, extremely hygroscopic syrup which is trans-

formed by hydriodic acid into methyl iodide and 3-methylhydan-
toin, m. p. 184—185°. The *barium* salt, $C_3H_2O_3N_2Ba$, is described.
It is converted by prolonged treatment with hot water into gly-
oxylurea.

Leucoturic acid has been further examined and is definitely
proved to be identical with oxalantin isolated by Limpricht by
the reduction of parabanic acid with zinc and dilute acid. (Since
the substance is shown to be a monobasic acid, the retention of
the name " leucoturic acid " is proposed.) The original formula,
$C_6H_6O_6N_4$, is confirmed. The substance forms ill-defined crystals,
m. p. 238°. It is acid towards litmus, and liberates carbon dioxide
from metallic carbonates. It is converted by solutions of alkali
hydroxides into oxalic acid and ammonia, and by concentrated
aqueous ammonia into ammonium oxalurate and dehydrohydan-
toate. It is oxidised by potassium dichromate to parabanic acid,
but does not yield hydantoin under the action of hydriodic acid
and phosphonium iodide. It is converted by diazomethane into
methyl dimethylleucoturate, ill-defined leaflets, m. p. 230° (decomp.),
in which one methyl group is shown to be attached to oxygen and
the other two groups to nitrogen. The constitution of the com-
pound is in all probability expressed by the formula

$$NH_2 \cdot CO \cdot N \colon CH \cdot CO \cdot NH \cdot CO \cdot NH \cdot CO \cdot CO_2H\,;$$
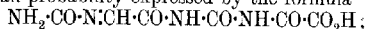
attempts to synthetise it from oxaluric acid and glyoxylurea were
not successful. H. W.

5-Hydroxy-1 : 3-dimethylhydantoin. HEINRICH BILTZ and
DOROTHEA HEIDRICH (*Ber.*, 1921, **54**, [*B*], 1829—1833).—The
substance has been prepared previously by Andreasch (A., 1882,
1054) by the reduction of 1 : 3-dimethylparabanic acid, and its
constitution has been established. The present investigation was
undertaken with the object of supplying further information
required in the investigation of glyoxylurea (preceding abstract).

Full details of an improved method for the isolation of dimethyl-
parabanic acid from caffeine are recorded and also for the crystallisa-
tion of 5-hydroxy-1 : 3-dimethylhydantoin; the latter has m. p.
70° after softening at 65°, b. p. about 283—284°. It is reduced by
concentrated hydriodic acid to 1 : 3-dimethylhydantoin, m. p.
45—46°. It is converted by benzoic anhydride into the correspond-
ing *benzoate*, small prisms, m. p. 122—123°, by phenylcarbimide
into the *phenylcarbamate*, m. p. 147—148° after softening at 145°,
and by diazomethane into 5-*methoxy*-1 : 3-*dimethylhydantoin*, which
could only be obtained on one occasion in the crystalline form. It
is oxidised by potassium dichromate to 1 : 3-dimethylparabanic
acid. H. W.

**Non-aromatic Diazonium Salts. VII. The Diazo-reaction
in the *iso*Oxazole Series.** GILBERT T. MORGAN and HENRY
BURGESS (T., 1921, **119**, 1546—1549).

Azides, Anthranils, and Azo-derivatives of Anthraquinone.
LUDWIG GATTERMANN and HANS ROLFES (*Annalen*, 1921, **425**,
135—161).—Anthraquinone-2-diazonium sulphate, on treatment

with hydrazine sulphate, yields 2-azidoanthraquinone, which shows no tendency to pass into an isomeride of 3 : 4-benzoyleneanthranil (Schaarschmidt, A., 1916, i, 856), a fact favouring Schaarschmidt's formula for the anthranil as against the "semiazo" formula of Gattermann and Ebert (A., 1916, i, 857).   2-Azidoanthraquinone, on condensation with ethyl acetoacetate, yields *ethyl* 1-β-*anthra-quinonyl-5-methyltriazole-4-carboxylate*, m. p. 201° (decomp.).

3 : 4-Benzoyleneanthranil may be obtained by treating anthra-quinone-1-diazonium sulphate with hydrazine sulphate, and 5. *nitro*-3 : 4-*benzoyleneanthranil* by nitrating 1-azidoanthraquinone by means of fuming nitric acid in the cold.   5-Nitro-3 : 4-benzoylene-anthranil forms brown needles, m. p. 244—245°, gives with con-centrated sulphuric acid a solution which on heating at 170° with boric acid becomes deep red and strongly fluorescent, and gives 1 : 4-diaminoanthraquinone on reduction by sodium sulphide.   It may also be prepared by the following series of reactions. 1-Nitro-4-aminoanthraquinone, when treated with nitrous acid and a salt of hydroxylamine, yields 4-*nitro*-1-*anthraquinoneazohydroxyl-amide*, $C_{14}H_7O_2N_2 \cdot NH \cdot OH$, unstable, red rhombs, which on heating with pyridine and acetic anhydride yields 4-*nitro*-1-*azido-anthraquinone*.   This substance, which forms yellow needles, on heating either alone or in benzene eliminates nitrogen and yields the nitrobenzoylencanthranil.

A solution of 4-nitro-1-anthraquinonediazonium sulphate on keeping gradually deposits red needles, termed by the authors "1 : 4-*anthraquinonequinonediazide*" (formula an-nexed).   On heating this with concentrated sul-phuric acid, quinizarine is produced.
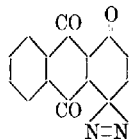
4-*Chloro*-1-*anthraquinoneazohydroxylamide* is prepared from 4-chloro-1-aminoanthraquinone. It crystallises from pyridine with 1 mol. of this substance, and passes into 4-*chloro*-1-*azidoanthra-quinone* on treatment with pyridine and acetic anhydride, or with pyridine formaldehyde and dilute aqueous sodium hydroxide.   4-Chloro-1-azidoanthraquinone on nitration yields 5-*chloro*-7-*nitro*-3 : 4-*benzoyleneanthranil*, yellow needles, which decompose at 187°.

1-*Anthraquinoneazohydroxylamide*-5-*diazonium sulphate*, bronze needles, is prepared from 1 : 5-diaminoanthraquinone, and on treat-ment with pyridine yields 1-N-*pyridyl*-5-*anthraquinoneazohydroxyl-amide*, red, lancet-like crystals, which with pyridine and acetic anhydride yields 3 : 4-o-N-*pyridylbenzoyleneanthranil*, golden-yellow, glistening leaflets, m. p. above 300°.

The following azo-compounds are described : p-1-*Anthraquinone-azodimethylaniline*, dark brown prisms, m. p. 249°.   p-1-*Anthra-quinoneazoaniline*, red needles, m. p. 211° (decomp.).   m-1-*Anthra-quinoneazo-p-toluidine*, deep red needles, m. p. 230°.   p-1-*Anthra-quinoneazophenol*, fiery red tablets.   p-1-*Anthraquinoneazoresorcinol* crystallises from aniline in red needles having 1 mol. of aniline. p-1 : 5-*Aminoanthraquinoneazoaniline*, red needles, m. p. 216°. p-1 : 5-*Anthraquinoneazohydroxylamideazodimethylaniline*, dark red

tablets containing 1 mol. of pyridine. (With pyridine and acetic anhydride it yields o-3 : 4-p-*dimethylanilineazobenzoyleneanthranil*, glistening, dark brown rhombs, m. p. 229°.) 1 : 1-*Anthraquinoneazo-β-naphthol*, fiery red needles, m. p. 290°. pp-1 : 5-*Anthraquinone-bisazoaniline*, red rhombs, decomposing at 251°. mm-1 : 5-*Anthra-quinonebisazo*-p-*toluidine*, dark red needles, m. p. 246° (decomp.). p-2-*Anthraquinoneazodimethylaniline*, needles having indefinite m. p. p-2-*Anthraquinoneazoaniline*, yellow needles. m-2-*Anthraquinone-azo*-p-*toluidine*, red rhombs, m. p. 227° (decomp.). p-2-*Anthra-quinoneazophenol*, bright red needles. 2-*Anthraquinoneazo*-β-*naphthol*, red needles, m. p. 250°. 4 : 2-*Anthraquinoneazo*-α-*naphthylamine*, needles, m. p. above 290°. *Ethyl* α-1-*anthraquinone-azoacetoacetate*, orange-yellow needles, m. p. 152° (*phenylhydrazone*, red needles, m. p. 263°). *Ethyl* α-2-*anthraquinoneazoacetoacetate*, small, yellow needles, m. p. 221° (*phenylhydrazone*, red rhombs, m. p. 247°). All these substances are prepared by coupling the anthraquinonediazonium salts with appropriate second components.

α-1-*Anthraquinoneazoacetoacetic acid*, yellow needles, m. p. 251°, is prepared by hydrolysis of the ester. On condensing with phenyl-hydrazine, it yields 4 : 1-*anthraquinoneazo*-1-*phenyl*-3-*methylpyrazol-one*, red needles, m. p. 252°. α-2-*Anthraquinoneazoacetoacetic acid*, small, yellow tablets, m. p. 247°, and 4 : 2-*anthraquinone*-1-*phenyl*-3-*methylpyrazolone*, bronze leaflets, m. p. 268°, are prepared in a similar manner. C. K. I.

The Proteins and Colloid Chemistry. JACQUES LOEB (*Science*, 1920, **52**, 449—456).—An address in which evidence is put forward that, as exhibited by the behaviour of the proteins, the chemistry of colloids does not differ from the chemistry of crystal-loids. It can be shown that ions combine with protein in the typical ratio in which the same ions combine with crystalloids only when it is recognised that the hydrogen-ion concentration of the protein solution determines the amount of ion combined with the protein, and the true comparison of one ion with another can only be made at the same hydrogen-ion concentration. The results of Hofmeister and of Pauli are invalid owing to non-observance of this condition. Only the kation or the anion, or neither, can combine with protein, according to the hydrogen-ion concentration of the solution. For example, gelatin at the isoelectric point, $p_{\mathrm{H}} = 4\cdot7$, combines with neither ion; at $p_{\mathrm{H}} > 4\cdot7$ only with kations (sodium gelatinate), at $p_{\mathrm{H}} < 4\cdot7$ only with anions (gelatin chloride). This can be shown when powdered gelatin, brought to various values for p_{H}, is treated on a filter with a neutral salt (for example, silver nitrate, nickel chloride, potassium ferrocyanide, and sodium thiocyanate) solution and the excess of salt washed away. It follows that values for both concentration and hydrogen-ion concentration are necessary to define a protein solution.

When acid is added to isoelectric gelatin (or other protein), equilibrium is established between acid, gelatin-acid salt, and isoelectric gelatin; when alkali is added, equilibrium is established between metal gelatinate, isoelectric protein, and hydrogen ions.

That the nature of the union is chemical is shown by the fact that three volumes of $0.1N$-phosphoric acid, or two volumes of $0.1N$. oxalic acid, or one volume of $0.1N$-hydrochloric, nitric, or sulphuric acid are required to bring a quantity of 1% gelatin solution to the same hydrogen-ion concentration. When this hydrogen-ion concentration is reached, the gelatin is in each case in combination with the same amount of acid, and the solutions show the same osmotic pressure. Analogous results are shown with bases, and with both bases and acids in the case of egg-albumin.

From these combining ratios the physical properties of proteins can be predicted. Any acid of which the anion behaves as a univalent ion raises the osmotic pressure, viscosity, and swelling of protein approximately twice as much as one of which the anion behaves as a bivalent ion; kations conform to the same rule. Curves in which the hydrogen-ion concentrations are plotted against the magnitude of certain physical properties (for example, swelling) indicate almost identical effects with chloride, bromide, nitrate, tartrate, succinate, citrate, and phosphate, with a minimum at $p_H = 4.7$ and a maximum at about $p_H = 3.2$; gelatin sulphate gives parallel curves, but the maximum value is only half that obtained previously. Protein salts with ions of the same valency show at the same hydrogen-ion concentrations like physical properties.   CHEMICAL ABSTRACTS.

Colorimetric Experiments on Tryptophan. IV. Formation of Melanoidin by the Acid Hydrolysis of Protein and its Dependance on Tryptophan Complexes. OTTO FÜRTH and FRITZ LIEBEN (*Biochem. Zeitsch.*, 1921, **116**, 224—231).—By investigating the tryptophan content of various proteins colorimetrically and determining the amount of melanoidin formed on acid hydrolysis, a parallelism is observed between the tryptophan content and the melanoidin. The authors consider that the melanoidins are the condensation products of the tryptophan molecules. The term humin is reserved for the results of change of carbohydrate complexes.   H. K.

Relation between the Salting-out and Precipitation-inhibiting action of Inorganic Ions on Protein Solutions. RICHARD LABES (*Pflüger's Archiv*, 1921, **186**, 112—125).—Inorganic ions influence the precipitation optimum of serum-albumin. With increasing concentrations of a neutral alkali salt the precipitation is displaced more and more into the region of higher acidity, up to the zone of the salting-out optimum. The neutral salts in extreme acid reactions salt out the best and the displacement of the precipitation optimum by the more strongly absorbed anions of the neutral alkali salts is to be found on the acid side.
                                          CHEMICAL ABSTRACTS.

Displacement of the Precipitation Optimum of Serum-albumin by Alkaloids, Dyes, and other Organic Electrolytes, and the Action of Non-electrolytes. RICHARD LABES (*Pflüger's Archiv*, 1921, **186**, 98—111).—The effect of various substances

on the precipitation of serum-albumin is twofold : (1) a displace-
ment of the precipitation optimum, and (2) an inhibition or activa-
tion of the precipitation. These actions are exerted by organic
salts in the form of chlorides just as by inorganic salts. Displace-
ment toward the less acid side increases with the kations in the
series : choline, physostigmine, morphine, pilocarpine, cocaine,
quinine, optochin, and cucupinotoxin. Displacement toward the
acid side increases with the anions in the series : resorcinol, phenol,
thymol, naphthol, salicylic acid, eosin, diamine-red. All the anions
investigated increase the precipitation more or less; inhibiting
anions, as the sulphate ion, are not found among the organic anions.
Non-electrolytes (ethyl, methyl, and heptyl alcohols; ethyl ether)
never cause a displacement but only a broadening of the precipita-
tion zone. Their effect is in striking parallel with their surface
activity. CHEMICAL ABSTRACTS.

Acerin : the Globulin of the Maple Seed. R. J. ANDERSON
[with W. L. KULP] (*J. Biol. Chem.*, 1921, **48**, 23—32).—The globulin
of the maple seed, isolated and purified by various methods, is found
to be a non-crystalline substance of the elementary composition : C,
51·44%; H, 6·80%; N, 18·34%; O, 22·87%; S, 0·55%. It closely
resembles arachin (A., 1917, i, 191), the globulin of the peanut, in
its composition and distribution of basic nitrogen; the figures
for the latter for acerin are : Cystine, 0·55%; histidine, 1·43%;
arginine, 10·07%; lysine, 6·07%. C. R. H.

Physico-chemical Examination of Hæmoglobin. State
of Aggregation of Hæmoglobin Molecules. M. CAMIS (*Folia
Hæmatologica* 2, 149—211; from *Chem. Zentr.*, 1921, iii, 418).—
The surface tension of dialysed hæmoglobin solutions, measured
stalagmometrically, decreases with rise of temperature and increases
with increase of concentration up to 6%. Addition of 0·006—0·1%
of lactic acid to a solution of hæmoglobin or laked blood diminishes
surface tension and lowers the extinction coefficient. Both effects
are attributable to a decrease in the number of particles. It is
supposed that the presence of lactic acid in blood leads to an
aggregation of hæmoglobin molecules. G. W. R.

Preparation and Analysis of Animal Nucleic Acid. P. A.
LEVENE (*J. Biol. Chem.*, 1921, **48**, 177—183).—Improved methods
for the preparation of nucleic acids from the spleen, pancreas, and
liver are described and analytical results given. For purposes
of estimation, the purine bases are separated in the form of their
hydrochlorides by alcoholysis of the nucleic acid. No confirmation
was obtained of the presence of mixed nucleic acids, that is, nucleic
acids containing both hexose and pentose nucleotides (cf. Feulgen,
this vol., i, 76). E. S.

The Structure of Thymus-Nucleic Acid and its Possible
Bearing on the Structure of Plant-Nucleic Acid. P. A. LEVENE
(*J. Biol. Chem.*, 1921, **48**, 119—125).—The author's ester formula
(A., 1920, i, 193) still expresses all the known facts about the
structure of yeast-nucleic acid. Jones's experiments (A., 1920, i,

687) on the rate of hydrolysis of yeast–nucleic acid are in agree-
ment with this formula, and not with the ether theory of union
by carbohydrates; they merely indicate that the union between
the four nucleotides is more labile than that between the phos-
phoric acid and carbohydrate. The fact that there is no change
in acidity during its hydrolysis by pig pancreas (Jones, A., 1920, i,
687) is due mainly to buffer effect.

From the hydrolysis product of thymus–nucleic acid, hexa-
thymidine diphosphoric acid and hexacytidinediphosphoric acid
were isolated by a simplified process and the barium salt of the
former was obtained in a crystalline condition. Under the experi-
mental conditions neither the monophosphoric nucleotides nor the
dinucleotide previously obtained (Levene and Jacobs, A., 1912, i,
926) could be isolated. The former are therefore probably secondary
products, while the existence of the latter is doubtful. In these
circumstances, and by analogy with yeast–nucleic acid, the following
structure for thymus–nucleic acid is suggested :

$$C_6H_{10}O_4\text{–O–}\overset{\overset{O}{\|}}{P}\text{–O–}C_6H_9O_3\text{–O–}\overset{\overset{O}{\|}}{P}\text{–O–}C_6H_9O_3\text{–O–}\overset{\overset{O}{\|}}{P}\text{–O–}C_6H_{10}O_4$$
$$\underset{C_5H_4N_5}{|}\quad\underset{OH}{|}\quad\underset{C_5H_5O_2N_2}{|}\quad\underset{OH}{|}\quad\underset{C_5H_4ON_5}{|}\quad\underset{OH}{|}\quad\underset{C_4H_4ON_3}{|}.$$

E. S.
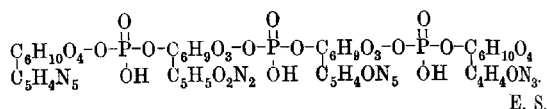
**Donnan Equilibrium and the Physical Properties of
Proteins. IV. Viscosity** (*cont.*). JACQUES LOEB (*J. gen.
Physiol.*, 1921, **4**, 73—95; cf. this vol., i, 693).—After completing
the proof that the viscosity of suspensions of powdered gelatin in
water is influenced by electrolytes in the same way as the viscosity
of solutions of gelatin, viscosity measurements are given to show
that solutions of gelatin contain (submicroscopic) particles of
solid jelly capable of swelling, and that the viscosity is due to
those. The viscosity of a solution of isoelectric albumin (which
exists in isolated molecules) changes linearly with the concentra-
tion, whilst gelatin, especially at low temperature, behaves in a
radically different manner. Experiments on the viscosity and
sedimentation of suspensions and solutions of casein chloride show
that particles of casein chloride occlude water in accordance with
a Donnan equilibrium between them and the surrounding liquid.
In a colloid solution in general there may be isolated ions and
molecules, giving rise to a general viscosity of low order, and
also (submicroscopic) particles, the volume of which changes in
accordance with the Donnan equilibrium, causing a high viscosity
which is markedly influenced by the P_H of the solution and by the
dissolved electrolytes.   W. O. K.

**The Reciprocal Relation between the Osmotic Pressure
and the Viscosity of Gelatin Solutions.** JACQUES LOEB (*J.
gen. Physiol.*, 1921, **4**, 97—112; cf. preceding abstract).—The
osmotic pressure of a gelatin suspension is due almost entirely to
the presence of free molecules of the gelatin, the viscosity to the
submicroscopic particles swollen in accordance with the Donnan

equilibrium. Thus in a solution of given concentration the larger the osmotic pressure the smaller the viscosity and vice versa. Experiments are described which verify this conclusion.

W. O. K.

Comparative Hydrolysis of Gelatin by Pepsin, Trypsin, Acid, and Alkali. JOHN H. NORTHROP (*J. gen. Physiol.*, 1921, **4**, 57—71).—The relative power of various hydrolysing agents to split protein linkings can be investigated by the following method. Gelatin partly hydrolysed by one agent is submitted to another, and hydrolysis, as indicated by "formal" titration, proceeds further than with either separately if they hydrolyse different linkings. On considerations such as this, it is found that linkings split by trypsin or pepsin are resistant to acid and easily hydrolysed by alkali; those split by pepsin are split by trypsin, although not necessarily vice versa; and of those split by both, rapid pepsin hydrolysis is associated with slow trypsin hydrolysis. W. O. K.

Invertase. RICHARD WILLSTÄTTER and FRITZ RACKE (*Annalen*, 1921, **425**, 1—135).—An examination of the conditions controlling the extraction of invertase from yeast is followed by a study of the adsorption of invertase from the yeast extract on kaolin, aluminium hydroxide and other substances, and the knowledge thus gained is applied to the preparation of invertase having a higher degree of purity than any yet obtained.

The extraction of invertase from yeast by digesting with water is by no means a purely physical process, some decomposition (autolysis), probably enzymatic, being necessary to bring about liberation of the invertase. For instance, the destruction of the yeast-cells by grinding with sand, although it facilitates the subsequent extraction, does not render the invertase immediately soluble.

The yield of invertase from a given specimen of yeast depends greatly on the past history of the latter; if it be dry yeast, the manner of drying is important. For instance, yeast dried at 100°, or by treating with acetone, gives poor yields of invertase. The chief factors which influence the speed of autolysis are dilution with water and the addition of antiseptics (for example, toluene, ethyl acetate, chloroform) both of which hasten the process. The addition of diammonium hydrogen phosphate, and neutralisation of the liquid by means of ammonia (the extracts as ordinarily prepared have an acid reaction) also have a similar although less pronounced effect.

The crude extract contains phosphates, precipitable by magnesium salts, and albumins, which may be removed by adding an excess of lead acetate, the lead being subsequently removed by passing hydrogen sulphide, and the residual acetic acid by dialysis.

When a limited amount of kaolin is added to the crude extract, adsorption of albumins occurs, but no appreciable amount of invertase is taken up. On the other hand, after the invertase has been purified by adsorption on aluminium hydroxide and subsequent extraction from the adsorbate, kaolin adsorbs it preferentially

and a further purification can thus be effected, the accompanying resins remaining in the mother-liquor.

Invertase is strongly adsorbed by aluminium hydroxide, even from aqueous solution, and still more strongly from an aqueous solution containing, say, 28% of acetone or of alcohol. A study of the fractional adsorption of invertase on aluminium hydroxide shows that at first certain impurities are taken up, and that only after an appreciable amount of aluminium hydroxide has been added does the invertase begin to be adsorbed in large quantities. In the later stages, the amount of invertase adsorbed by a given weight of aluminium hydroxide diminishes asymptotically in such a manner that in preparing the adsorbate for the purpose of purifying the invertase it is often convenient to leave about 10% in the mother-liquor.

The invertase cannot be extracted from the adsorbate by pure water, or by water charged with carbon dioxide. With a concentrated aqueous solution of sucrose, the adsorbate behaves just as though the invertase which it contains were free, and, since the quantity of invertase in a solution is always estimated by means of its activity towards sucrose, this property of the adsorbate affords a means of examining its stability. It is found that a decided loss of activity occurs on keeping. Almost quantitative extraction can be effected by means of 1% aqueous disodium hydrogen phosphate, 1% aqueous diammonium hydrogen phosphate, 0·04% aqueous ammonia, 1% ammonium oxalate, very dilute sodium carbonate, and aqueous pyridine.

It is a curious fact that when the original yeast extract is prepared without the addition of ammonium hydroxide a preliminary purification by precipitation with lead acetate hinders the extraction by ammonia of the invertase from its adsorbate with aluminium hydroxide, whilst if neutral extracts, obtained with the aid of ammonia, be employed a preliminary treatment with lead acetate appears to be necessary to ensure successful extraction by ammonia.

Invertase is adsorbed by normal calcium phosphate $(Ca_3P_2O_8)$, but conversion of this into calcium hydrogen phosphate $(CaHPO_4)$ renders extraction possible.

A solution in water of invertase which has reached a certain degree of purity gives a precipitate with uranyl acetate. If sufficient uranyl acetate be employed this precipitate contains the whole of the invertase originally present in the solution. Extraction takes place in 0·01N-aqueous sodium carbonate.

Using the above facts methods are detailed in the original for the preparation of invertase.

Invertase decomposes gradually in aqueous solution, loss of activity being complete in one and a half years, and fairly quickly in the presence of more than a limited quantity of alcohol or acetone. It undergoes a temporary loss of activity on drying.   C. K. I.

Action of Emulsin from Almonds on Lactose in Solution in 85% Ethyl Alcohol.

Marc Bridel (*Compt. rend.*, 1921, **173**, 501—504).—From the products of the action of emulsin on a

0.2% solution of lactose in 85% alcohol at the ordinary temperature, ethyl β-galactoside was isolated. The lactose is thus first hydrolysed and then the galactoside is synthesised. W. G.

Lead Triaryl, a Parallel to Triphenylmethyl. II. Lead Tricyclohexyl. ERICH KRAUSE (*Ber.*, 1921, **54**, [*B*], 2060—2066; cf. Krause and Schmitz, A., 1920, i, 197).—The preparation of lead tricyclohexyl as a crystalline substance the molecular weight of which in dilute solution corresponds exactly with that required by the formula $(C_6H_{11})_3Pb$ places beyond doubt the existence of organo-derivatives of tervalent lead. The substance has the unusual property of uniting with iodine in benzene solution at the ordinary temperature to form lead tricyclohexyl iodide with such readiness that it may be estimated quantitatively in this manner, whereas when warmed with an excess of iodine it loses a cyclohexyl group and yields lead dicyclohexyl di-iodide. Since lead tetracyclohexyl can only be produced with great difficulty, it is obvious that the formation of lead triaryls depends on the molecular volume of the radicle introduced rather than on its chemical nature.

[With G. S. REISSAUS.]—*Lead tricyclohexyl*, thin, yellow, hexagonal platelets, decomp. 195°, is prepared by the gradual addition of finely-divided lead chloride to a solution of magnesium cyclohexyl bromide in dry ether; in substance or when dissolved in benzene, it is very sensitive to the action of light, but the dry compound can be preserved indefinitely in the dark. *Lead tricyclohexyl iodide*, $Pb(C_6H_{11})_3I$, crystallises in long, golden-yellow, rhombic prisms, m. p. 91·7°; it is converted by aqueous potassium hydroxide solution into *lead tricyclohexyl hydroxide*, which could only be isolated as a white, amorphous powder. *Lead tricyclohexyl chloride*, pale yellow, slender needles, decomp. about 236°, and *lead tricyclohexyl bromide*, straw-yellow needles, decomp. about 210°, are also described. *Lead dicyclohexyl di-iodide*, $Pb(C_6H_{11})_2I_2$, crystallises in pale yellow needles, decomp. about 98°, and is somewhat unstable, whereas the corresponding *dibromide* forms pale yellow needles, decomp. about 142°. *Lead tetracyclohexyl*, colourless, rectangular platelets, which become yellow at 130° and blacken at 160°, is prepared by the protracted action of an ethereal solution of magnesium cyclohexyl bromide on lead tricyclohexyl bromide. H. W.

Improvements relating to Soluble [Organic] Mercury Compounds. J. D. RIEDEL AKT. GES. (Brit. Pat. 161922).— Hydroxymercurisalicylic anhydride (170 grams), suspended in water, is treated with potassium cyanide (37 grams) and the amorphous mercury compound is rapidly converted into a crystalline mass, which, when a considerable amount of water is present (for example, 800 grams) consists of the potassium salt of the *o*-cyanomercurisalicylic acid. With a lesser quantity of water (500 grams), the product consists of a mixture of this substance with the corresponding *para*-compound, which may be isolated by

extracting the crystalline mass obtained after filtering off the coloured mother-liquor and washing with aqueous alcohol, with about three times its weight of water at 25°, and cooling the extract to 0°, when a woolly mass of crystals separates and is purified by recrystallisation from hot water. The pure ortho-compound forms colourless, short prisms with a satin lustre, soluble in about 25 parts of water at ordinary temperatures with a neutral reaction. The pure para-compound forms oblong tables about four times as soluble in water as its isomeride. The solution has an acid reaction and darkens with ammonium sulphide more rapidly than the ortho-isomeride. Both compounds give with silver nitrate a silver salt of the formula $CN \cdot Hg \cdot C_6H_3(OH) \cdot CO_2Ag$.

<div align="right">G. F. M.</div>

Organo-chromium Compounds. I. Chromium Penta-phenyl Hydroxide. FRANZ HEIN (*Ber.*, 1921, **54**, [*B*], 1905– 1938).—A detailed account of investigations, a preliminary notice of which has appeared previously (A., 1919, i, 232). Chromium pentaphenyl bromide, $CrPh_5Br$, is obtained as an orange-brown, amorphous substance by the action of an ethereal suspension of chromic chloride on a well-cooled ethereal solution of magnesium phenyl bromide. The product is doubtless a mixture of substances and the yields are not good; its purification is rendered exceptionally difficult by its sensitiveness towards air, light, rise of temperature, and acids, and by its persistently amorphous nature. With alcoholic mercuric chloride solution, the crude product yields a mercurichloride, $CrPh_5Br,HgCl_2$, which can be purified by repeated extraction with boiling alcohol, under which it melts to a product resembling sealing-wax. The latter appears to be homogeneous, but is still less stable than the crude bromide. From it, it has been found possible with difficulty to prepare the *compound,*

$$2CrPh_5Br,Et_2O,$$
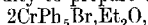
an amorphous powder which softens at about 80° and has m. p. about 100° (decomp.). A similar crude chromium pentaphenyl bromide can be obtained from chromyl chloride and magnesium phenyl bromide in the presence of well-cooled benzene (cf. Sand and Singer, A., 1904, i, 38), but not from chromic oxide. The production of the compound from a derivative of hexavalent chromium renders it probable that the reaction with chromic chloride takes place in accordance with the scheme $4CrCl_3+ 5MgPhBr \longrightarrow CrPh_5Br+2MgBr_2+3MgCl_2+3CrCl_2$, which would account for the poor yield of the organochromium product.

The bromine atom of chromium pentaphenyl bromide is displaced with unusual readiness, for example, when its solution in chloroform is agitated with an aqueous suspension of silver oxide, whereby the chromium pentaphenyl hydroxide passes into the aqueous layer. Since the other chromium compounds present in the crude bromide remain dissolved in the chloroform, a ready method of preparing the hydroxide seemed to be indicated; these hopes were not, however, fulfilled, since it was found that the silver oxide also exerted an oxidising action, and that a mixture of

bases resulted which decomposed with extreme readiness and from which it was not possible to prepare solid or crystalline salts with the possible exception of the perchlorate. The strength of chromium pentaphenyl hydroxide inhibits its production by the use of potassium hydroxide in the usual manner, but, by reason of the insolubility of potassium bromide in alcohol, this can be achieved by working with the latter solvent. For this purpose, alcoholic solutions of the crude bromide and potassium hydroxide are mixed, diluted with ether, and filtered from the precipitated potassium bromide; the filtrate is concentrated, and the well-cooled residue is treated with chloroform or anisole to remove excess of potassium hydroxide. The clear solution is shaken with ice-cold water into which the chromium phenyl bases gradually pass and from which *chromium pentaphenyl hydroxide* separates in the form of golden-yellow leaflets or prismatic needles. The substance is best preserved over potassium hydroxide solution (30%) and under diminished pressure. When prepared under these conditions (which correspond with air-drying), the substance loses $2H_2O$ when placed over calcium chloride and a further $2H_2O$ in the presence of phosphoric oxide (in the latter process the colour changes from brownish-orange to a dark olive-brown). Its constitution is therefore expressed by the formula

$$[CrPh_5(OH)_2]OH,2H_2O.$$
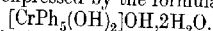
The completely dehydrated substance decomposes somewhat readily when preserved at the ordinary temperature, with the production of diphenyl; a similar but slower change occurs with the dihydrate. The anhydrous base and its dihydrate can be re-hydrated to the tetrahydrate. When placed over concentrated sulphuric acid, the substance loses 2% of water and yields an orange-coloured product, the analyses of which give results agreeing with those required by the dihydrate of chromium pentaphenyl hydroxide; this cannot be dehydrated further over phosphoric oxide (the *modification* is termed the β-base). Comparison of the electrical conductivities of chromium pentaphenyl hydroxide, sodium hydroxide, and ammonia in absolute methyl-alcoholic solution proves the former to be a very strong base; in aqueous methyl-alcoholic solution the conductivity of the former does not appear to approach a limiting value with increasing dilution, a peculiarity for which a satisfactory explanation is not at present forthcoming. The ultra-violet absorption spectrum has been measured in absolute ethyl alcoholic solution and found to be closely similar to that of solutions of chromic acid and dichromates, but the absorption is noticeably greater in the case of the base than in those of the acid or salts.   H. W.

Physiological Chemistry.

Acidosis. XVII. The Normal and Abnormal Variations in the Acid-Base Balance in the Blood. DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1921, **48**, 153—176).—This paper is a review of recent work on the subject of the regulation of the reaction of the blood. For purposes of illustration, a diagrammatic repre. sentation is adopted of the different conditions which may arise as the result of variations in the acid-base ratio. These conditions together with the compensatory measures employed by the body to meet them, are discussed at some length.

Further, the question of the relation of the acid–base balance of the blood to that of the other body-fluids, and the question of the available alkali of the blood, are considered, and a brief reference is made to methods which have been suggested for the determination of the state of the acid–base balance.   C. R. H.

The Potassium Content of Normal and some Pathological Human Bloods. VICTOR C. MYERS and JAMES J. SHORT (*J. Biol. Chem.*, 1921, **48**, 83—92).—Figures are given for the amount of potassium present in human serum and whole blood under normal and various pathological conditions. The estimations were made by the cobaltinitrite method, and the precautions essential to the success of the analysis are discussed.   C. R. H.

Calcium in the Blood of Children. W. DENIS and F. B. TALBOT (*Amer. J. Diseases Children*, 1921, **21**, 29—37).—By a modification of Lyman's nephelometric method the following results, expressed in mg. of calcium per 100 c.c. of plasma, were obtained : normal adults, 7·2 to 12·1 (average 10); children (8—10 months old) suffering from acute rickets, less than 2 to 8; children (6 months to 4 years) convalescent, 4·5 to 11·2; tetany cases (4 – 22 months), 1 to 7·7; cases of convulsions without tetany, 3·2 to 8·2; epilepsy cases, 3 to 9; chorea cases, 4·8 and 6; pneumonia cases (6 months to 7·5 years), less than 2 to 12·1. In a number of cases the magnesium was also estimated.
          CHEMICAL ABSTRACTS.

The Amount of Amino-acids in Blood. K. DE SNOO (*Diss. Utrecht*, 1920, 130 pp.; from *Physiol. Abstr.*, 1921, **6**, 368).—The amount of nitrogen due to amino-acids in human blood is, on an average, 6·8 mg. per 100 c.c. This amount increases after a protein meal, as also does the amino-acid content of the urine. Absorption of amino-acids probably ceases six hours after a meal. Details of the variation of the amino-acid content of the blood in cases of certain diseases are given.   E. S.

Colorimetric Experiments on Tryptophan. V. The Proteins of Immune Sera and their Tryptophan Content. OTTO FÜRTH and FRITZ LIEBEN (*Biochem. Zeitsch.*, 1921, **116**, 232—236).—Sera from horses immunised against diphtheria, dysentery,

and tetanus showed an increased content of sera protein due to an increase in the ψ-globulin fraction. The content of tryptophan in each fraction was, however, normal.　　　H. K.

Photosynthetic Processes in the Air, upon the Land, and in the Sea in Relation to the Origin and Continuance of Life on the Earth. Hugo Müller Lecture, delivered before the Chemical Society on June 16th, 1921. BENJAMIN MOORE (T., 1921, 119, 1555—1572).

Dietary Factors influencing Calcium Assimilation. I. The Comparative Influence of Green and Dried Plant Tissue, Cabbage, Orange Juice, and Cod-liver Oil on Calcium Assimilation. E. B. HART, H. STEENBOCK, and C. A. HOPPERT (J. Biol. Chem., 1921, 48, 33—50).—The calcium balance of dry and lactating goats is positive on a diet of green oats and negative on one of dry oat straw. It is therefore concluded that the former diet contains a dietary factor which facilitates calcium assimilation. The same factor is present in cod-liver oil but absent in raw or dried cabbage. Experiments with orange juice did not lead to consistent results (cf. also Steenbock and Hart, A., 1913, i, 550; Meigs, Blatherwick, and Cary, A., 1920, i, 203).　　　E. S.

The Behaviour of the Residual Nitrogen of Egg-white and of Yolk on Incubation. MASAJI TOMITA (Biochem. Zeitsch., 1921, 116, 12—14).—After removal of all substances precipitable by boiling dilute acetic acid and by tannic acid solution, the author determined the total residual nitrogen in the filtrate by Kjeldahl's method, the nitrogen in the fraction still precipitable by phosphotungstic acid by Kjeldahl's method, and the amino-nitrogen in the final filtrate by van Slyke's method. Fresh eggs contain very little residual nitrogen or amino-nitrogen, but as incubation proceeds there is a steady increase of residual nitrogen up to fourteen days.
　　　H. K.

Behaviour of Dextrose added to the White of Eggs during Incubation. MASAJI TOMITA (Biochem. Zeitsch., 1921, 116, 22—27).—The normal content of dextrose in eggs after three days' incubation is 0·43% in the egg-white and 0·2% in the yolk. Addition of dextrose to the white of fresh eggs followed by incubation for three days causes a marked disappearance of dextrose from the egg-white, but not from the yolk. Dextrose appears therefore to be a source of the lactic acid produced.　　　H. K.

The Formation of d-Lactic Acid in the Animal Organism. MASAJI TOMITA (Biochem. Zeitsch., 1921, 116, 1—11).—Quantitative experiments on eggs show that the d-lactic acid content is very small and of the order 0·006% in egg-white and 0·01% in the yolk. The lactic acid content of unfertilised is less than that of fertilised eggs and, as incubation proceeds, the lactic acid reaches its maximum on the fifth day and becomes very small at the end of a fortnight.　　　H. K.

The Influence of the Addition of Dextrose and Alanine to Egg-white on the Formation of *d*-Lactic Acid during Incubation. MASAJI TOMITA (*Biochem. Zeitsch.*, 1921, **116**, 15—21).— Dextrose and alanine were separately added to the white of an egg and the egg incubated for three days. Alanine had no marked effect on the lactic acid content of egg-white or yolk, but dextrose produced an increase in the lactic acid content of egg-white somewhat less than 100%.   H. K.

The Formation of Sarcolactic Acid in the Animal Organism. The Formation of *d*-Lactic Acid by the Autolysis of Hen's Eggs. MASAJI TOMITA (*Biochem. Zeitsch.*, 1921, **116**, 28—39).—The lactic acid content of egg-white undergoing autolysis is independent of time, but that of the yolk increases considerably and eventually falls off. If dextrose is added to yolk, the lactic acid shows an enormous increase, whilst that of the egg-white is unchanged. Alanine has no effect in either case. During autolysis, an enzyme present in the yolk, but not in the egg-white, has the power of converting dextrose into lactic acid.   H. K.

Chemical Composition of the Egg-shell of the Silkworm Moth. MASAJI TOMITA (*Biochem. Zeitsch.*, 1921, **116**, 40—47).— The egg-shell of the silkworm moth is composed of protein and not of chitin. On hydrolysis with acids and separation of the amino-acids by the standard methods, 40% of the constituent amino-acids was isolated. Glycine, 13·7%, and tyrosine, 11·2%, were present in the largest proportion.   H. K.

Can the Chloridion of Ringer Solution be Replaced by other Ions with the beating Frog's Heart ? E. R. O. FINCKH (*Biochem. Zeitsch.*, 1921, **116**, 262—265).—An isolated frog's heart continues to beat when all chloridion is replaced by bromidion. The substitution by the iodide ion or by the nitrate ion exerts a harmful effect owing to formation of iodine or nitrite.   H. K.

Conditions for the Precipitation of the Wassermann Reaction Antigen (Heart Extract). RUDOLF MÜLLER (*Biochem. Zeitsch.*, 1921, **116**, 215—223).—When an alcoholic extract of ox-heart is added to sodium chloride solutions of various concentrations, a colloidal solution is primarily obtained, further addition of the alcoholic solution leading to precipitation. The higher the initial concentration of the saline solution the smaller the quantity of the alcoholic heart-extract necessary to produce precipitation.   H. K.

The Selective Absorption of Potassium by Animal Cells. I. Conditions Controlling Absorption and Retention of Potassium. PHILIP H. MITCHELL and J. WALTER WILSON (*J. gen. Physiol.*, 1921, **4**, 45—56).—The potassium content of the muscles of frogs decreases by 8 to 15% during perfusion with a potassium-free Ringer solution, but this loss may be due entirely to the presence of a potassium-free medium. There is no additional

loss of potassium if the muscle is stimulated during the perfusion, but a larger loss occurs if stimulation is carried so far as to cause loss of irritability. Probably this is connected with the fact that a contracting muscle more readily takes up rubidium and cæsium than a resting one.   W. O. K.

Chemical and Physical Properties of Muscle and Muscle Extracts. VII. Fats, Cholesterol, and Lipoids in the Extract from Striped Muscle of Dogs. G. QUAGLIARIELLO (*Arch. internat. Physiol.*, **16**, 239—250; from *Chem. Zentr.*, 1921, iii, 568).—The extract was obtained from the muscle of fasting dogs, using a Buchner press. After separation of fat by centrifuging, the extract was warmed with an equal volume of 1% sodium chloride for thirty minutes at 45° and then placed in an ice-chest for twenty-four hours, whereby myosin separated in granular form. This was removed by centrifuging and the myoprotein remaining in solution separated by coagulation. The myosin was examined quantitatively for ash, total nitrogen, total fatty acids, unsaponifiable fat (cholesterol), and lipoid phosphorus. In the case of the myoprotein, total nitrogen, total acid, and cholesterol were estimated. Of the total fatty acids and cholesterol in the fat-free extract, 90% occurred in the myosin granules. Of the fatty acids in myosin, half is associated with phospholipoids. The author concludes that the myosin granules (and consequently the fibrillæ) consist of lipoid substances, although no constant relationship was found between the total nitrogen and the total fatty acids of the myosin granules, as might be expected from this hypothesis (cf. A., 1913, i, 1132).   G. W. R.

Do Subminimal Stimuli influence the Course of Chemical Changes in Muscle? JAKOB K. PARNAS and EMILIA LASKA-MINTZ (*Biochem. Zeitsch.*, 1921, **116**, 59—70).—Contrary to the findings of Heidenhain and Gottschlich (*Pflüger's Archiv*, 1894, **56**, 355), the subminimal stimulation of frog's muscle failed to produce any increase in the normal lactic acid content or in the degree of acidity. The lactic acid was estimated by Parnas's modification of the method of von Fürth and Charnass (*Zentr. Physiol.*, 1915, **30**, 1), an important simplification being the extraction of the lactic acid by grinding the muscle with quartz sand and saturated ammonium sulphate at −10°.   H. K.

Carbohydrate Metabolism of Isolated Amphibian Muscle. JAKOB K. PARNAS (*Biochem. Zeitsch.*, 1921, **116**, 71—88; cf. A., 1914, i, 772).—Details are given for the estimation of the carbohydrate content of 0·5 to 1·5 grams of muscle. Using this method, the author has investigated the relation between the carbohydrate consumption of muscle stimulated to maximum contraction several thousand times and the work done by it. The efficiency of the gastrocnemius is 35% and the sartorius 50%. The latter value agrees with that found by Hill (*Ergebnisse Physiol.*, 1916, **15**, 341).
                                                         H. K.

The Carbohydrate Metabolism of Isolated Amphibian Muscle. The Exchange in the Muscle of Pancreas-diabetic Animals. JAKOB K. PARNAS (*Biochem. Zeitsch.*, 1921, **116**, 89—101; cf. A., 1914, i, 772).—Experimental glycosuria was produced by removal of the pancreas from water-frogs. The carbohydrate consumption of the resting muscle and the amount of lactic acid formed in resting muscle and in heat-rigor muscle was the same as that of normal muscle. The same applies under anærobic conditions. The oxygen consumption of the muscle of the pancreas-free frog was the same as that of normal muscle, but the mechanical efficiency was somewhat less. The metabolism of the muscles of diabetic animals is thus identical with that of normal muscle.   H. K.

Mechanical Efficiency of the Combustion Processes occurring in Isolated Amphibian Muscle. JAKOB K. PARNAS (*Biochem. Zeitsch.*, 1921, **116**, 102—107).—By means of an apparatus which is pictured and fully described, the oxygen consumption of the gastrocnemius muscle of the frog, whilst undergoing a great number of contractions, was measured over a period of several hours. The work done by the muscle compared with that calculated from the oxygen consumption showed a mechanical efficiency of 44%. This agrees closely with the efficiency determined from the consumption of carbohydrate by the sartorius muscle. The only source of energy in isolated muscle is therefore the carbohydrate.   H. K.

Proteins of the Muscle of *Haliotis gigantea*, Gmelin. EIJI TAKAHASHI (*J. Chem. Soc. Japan*, 1921, **42**, 537—545).—Crushed pieces of the muscle of the ear-shell, *Haliotis gigantea*, were boiled with water, the insoluble part was treated with alcohol and ether and dried; it contained water 4·02%, ash 6·40%, and total nitrogen 14·236%. One hundred and twenty grams of the dried sample were hydrolysed by boiling with 360 grams of 25% sulphuric acid during ten hours and the following monoamino- and diamino-acids were isolated (in grams) : cystine 4·3, tyrosine 5·6, glutamic acid 12·4, alanine 1·2, leucine 18·0, proline 2·7, serine 2·3, aspartic acid 3·8, arginine 6·4, hystidine 0·4, and lysine 3·4 grams. Glycine was not present, and the presence of phenylalanine and valine is doubtful.   K. K.

The Distribution of Urea in the Organism. K. L. GAD-ANDRESEN (*Biochem. Zeitsch.*, 1921, **116**, 266—302).—A complete study of the amount of urea in the various parts of the body. The distribution coefficient of urea between plasma and corpuscles and between Ringer solution and corpuscles is between 0·72 and 0·8. Between plasma and the various secretions the coefficient is unity, whilst between plasma and water-free fat it is 0·07. The concentration of urea is the same in all tissues and in the blood, with the exception of the fatty tissues. The concentration of ammonia is the same in the blood, the secretions, and the various organs.   H. K.

The **Metabolism of Amphibian Larvæ.** Jakob K. Parnas and Zofia Krasinska (*Biochem. Zeitsch.*, 1921, **116**, 108—137).— The oxygen consumption of the larvæ of frogs was determined from the moment of fertilisation and on through the early stages of growth. The influence of the proportion of oxygen, and of the presence of urethane, was also investigated. In general, over the whole period of growth there is a progressive increased consumption of oxygen, although over short periods of evolution of the larvæ the oxygen consumption may be constant. The paper is fully illustrated by graphs and figures.   H. K.

The **Fat of *Caballus equus.*** A. Heiduschka and A. Steinruck (*J. pr. Chem.*, 1921, **102**, 241—266).—The material under investigation was a mixed product obtained from the various fatty tissues of the horse; it had m. p. 32·3°, d^{15} 0·9224, d^{25} 0·9135, n_D^{40} 1·4617, acid value, 2·62, saponification value, 203·95, Reichert-Meissl value, 0·417, Polenske value, 0·375, iodine value, 75·17, acetyl value, 14·02, saponification value after acetylation, 6·93.

The liquid fatty acids contain, in addition to oleic acid, 7·34% of linolic acid and 1·61% of linolenic acid. Farnsteiner found 9·9% of linolic acid, but the difference is explained by the fact that he calculated the content from the iodine value of the unsaturated acids obtained from the kidney fat, whereas the author employed an average sample of the total fat. Varrentrapp's method for the separation of the solid and liquid acids does not give exact values; better results are obtained by the precipitation of an ethereal solution of the total fatty acids with alcoholic lead acetate solution.

The solid fatty acid does not consist of heptadecoic acid, but of a mixture of palmitic and stearic acids; this result is confirmed by three independent methods of analysis.

The total fatty acids are composed of linolenic acid 1·69%, linolic acid, 6·68%, oleic acid, 55·24%, stearic acid 6·82%, palmitic acid 29·47%. In addition, 0·426% of unsaponifiable matter, mainly cholesterol, is present.   H. W.

Glycerides of Goose Fat. Conrad Amberger and Karl Bromig (*Pharm. Zentr.-h.*, 1921, **62**, 547—548).—Goose fat when kept for some time deposits about 15% of solid fat (iodine number, 52·5) containing α-stearodipalmitin, m. p. 57·4°, and β-stearodipalmitin, m. p. 63·0°; 100 c.c. of ether at 15° dissolve 1·32 grams of the former and 0·90 gram of the latter. The liquid portion of the fat (iodine number 77·0) consists chiefly of triolein, and both solid and liquid portions contain a quantity of oleodipalmitin, m. p. 33·5°.   W. P. S.

Chemical Investigation of Mutton-bird Oil. I. C. L. Carter (*J. Soc. Chem. Ind.*, 1921, **40**, 220T).—Mutton-bird oil is extracted from the stomach of an Australian petrel, *Aestrelata lessoni*. It resembles sperm oil very closely in its physical and chemical properties. The alcohols obtained by saponification of the oil consist chiefly of cetyl alcohol, and the greater portion of the mixed fatty acids consists of oleic acid. There is evidence of the presence of acids of the linolic or linolenic series,   W. G.

Chemical Study of (I), certain Pacific Coast Fishes; (II), the California Sardine (*Sardinia cœrulea*). D. B. DILL (*J. Biol. Chem.*, 1921, **48**, 73—82, 93—103).—Large variations were found in the fat content of the fishes studied. These variations could not, usually, be correlated with any other factor, although in many cases the maximum fat content was found in the summer months.   E. S.

Formation and Excretion of Hippuric Acid in Man. I. SNAPPER (*Nederl. Tidschr. Geneesk.*, 1920, **65**, 3044; from *Physiol. Abstr.*, 1921, **6**, 377).—Hippuric acid in amounts up to 300 mg. daily was found in the urine of persons on a milk diet. The source of the benzoic acid necessary for its formation is probably phenyl-alanine, produced by the digestion of proteins. In men with normal kidneys, 5 grams of sodium benzoate were almost completely excreted in the form of hippuric acid within twelve hours. From a study of certain pathological cases the conclusion is drawn that the glycine depot of the body is not dependent on the bile secretion.
                                           E. S.

Amino-nitrogen in the Urine as indicated by the Formol Method. C. CIACCO (*Arch. sci. med.*, 1920, **43**, 177—181).—The author considers that the amino-nitrogen indicated by the formol method in urine is not present in the form of simple amino-acids, but as more or less complex polypeptides. The discordant results commonly obtained are thus explained, since polypeptides are partly precipitated by salts of heavy metals or by phosphotungstic acid. In order to study the elimination of the more or less complex protein fragments in various pathological conditions, it is suggested that the formol method should be applied (*a*) after hydrolysis of the urine without any preliminary treatment, (*b*) after treatment with tannin and lead acetate, or with mercuric acetate, and (*c*) after hydrolysis of the filtrate obtained by precipitation with these substances.   CHEMICAL ABSTRACTS.

The Local Anæsthetic Properties of Benzoylcarbinol. A. M. HJORT and C. E. KAUFMANN (*Proc. Soc. Exp. Biol. Med.*, 1920, **17**, 79—80).—Benzoylcarbinol possesses local anæsthetic properties which in general are superior to those of benzyl alcohol, α-methylbenzyl alcohol, or phenylethyl alcohol. Benzoylcarbinol is less irritant to the body-tissues than these compounds, and is the most stable of the series. Its solubility in water is sufficient to make it a practicable local anæsthetic.   CHEMICAL ABSTRACTS.

Methylation in the Animal Organism. I. Methylation of Pyridine in the Organism of the Rabbit. MASAJI TOMITA (*Biochem. Zeitsch.*, 1921, **116**, 48—54).—Contrary to the findings of Abderhalden and his co-workers, rabbits on various diets can convert pyridine to a small extent into methylpyridine, which was isolated as the platinum salt.   H. K.

Methylation in the Animal Organism. II. The Site of the Methylation of Pyridine in the Animal Organism. MASAJI TOMITA (*Biochem. Zeitsch.*, 1921, **116**, 55—58).—Extirpation of

the spleen or pancreas in frogs has no influence on the production of methylpyridine, whilst removal of the liver completely inhibits it. In dogs, removal of the testicles or spleen has no influence on the production of methylpyridine. The methylation is assumed to take place in the liver, but experiments with isolated organs have not so far been successful.　　H. K.

Biological Action of Proteinogenous Amines. A Contribution to the Question of the Acetonitrile Reaction. O. WUTH (*Biochem. Zeitsch.*, 1921, **116**, 237—245).—Hunt (A., 1905, ii, 847) showed that the toxicity to mice of acetonitrile is greatly diminished by previous administration of thyroid substance. The author finds that tyramine and di-iodotyramine can likewise protect mice against acetonitrile. Histamine is, however, without action.　　H. K.

The Toxicity of Acids to Infusoria. II. and III. M. E. COLLETT (*J. Exp. Zool.*, 1921, **34**, No. 1; from *Physiol. Abstr.*, 1921, **6**, 353, 354).—II. The addition of hydrochloric acid to solutions of organic acids does not yield conclusive evidence as to the toxicity of the molecule. Mixtures of certain acids (formic, acetic, butyric, valeric, benzoic, salicylic, with Paramœcium and Euplotes, and citric with Euplotes only) with their sodium salts are more toxic than can be accounted for by the P_H of the mixture or the toxicity of the salts. This seems to indicate that the molecules of these acids are in themselves toxic. There is no evidence of toxicity of the anion or the molecule in lactic, succinic, or tartaric acid at the concentrations used. The relative toxicity of $0.01 M$-solutions of the sodium salts is as follows : Paramœcium—salicylate, benzoate, tartrate, succinate, citrate, formate, acetate, butyrate, valerate, chloride, lactate; Euplotes—citrate, salicylate, benzoate, tartrate, succinate, formate, chloride, acetate, butyrate, valerate, lactate.

III. Length of life in solutions of various acids is extended by the addition of inorganic chlorides. The acids tested fall into two groups : the first includes hydrochloric, formic, acetic, succinic, lactic, tartaric, citric; the second butyric, hexoic, benzoic, salicylic, phenylacetic. The relative antagonistic power of the chlorides is set out. Sodium chloride increases the antagonistic power of barium and magnesium chlorides against all acids, but that of calcium and strontium chlorides only against acids of the second group. The action of the salts is probably double. Each has some influence on phase reversal, and thus on the rate of penetration of the acid; and each also stabilises the cell colloids against the swelling or coagulative action of the H-ion.　　E. S.

Chemistry of Vegetable Physiology and Agriculture.

Fermentation Process for the Production of Acetone, Alcohol, and Volatile Acids from Maize Cobs. W. H. PETERSON, E. B. FRED, and J. H. VERHULST (*J. Ind. Eng. Chem.*, 1921, **13**, 757—759).—When maize cobs are heated under a pressure of 20 lb. per square inch with about four times their weight of water and 8% of their weight of sulphuric acid, they yield from 25 to 30% of reducing sugars, chiefly xylose. The crude xylose syrup obtained is fermented readily and almost completely by *Bacillus aceto-ethylicum*; 100 lb. of maize cobs yield 2·7 lb. of acetone, 6·8 lb. of alcohol, and 3·4 lb. of formic and acetic acids. During the fermentation an excess of calcium carbonate must be present to neutralise the acids as they are formed.   W. P. S.

The Manufacture of Nitrates by the Biochemical Oxidation of Ammonia. E. BOULLANGER (*Ann. Inst. Pasteur*, 1921, **35**, 575—602).—A description of large-scale laboratory experiments designed to determine the best conditions for the preparation of nitrates by the biochemical oxidation of ammonium salts in solutions percolating through peat or some other material charged with nitrifying organisms.

In the first stages a 0·25% solution of ammonium sulphate should be used percolating at the rate of 20—40 litres per cub. metre of peat per day. When the organisms have spread throughout the mass, this amount may be gradually increased to 200 litres of 0·75% solution. The presence of nitrates at the commencement checks the multiplication of the nitrifying organisms. Later on, ammonium nitrate, obtained by the interaction of the calcium nitrate previously formed and ammonium carbonate, may be used. It is preferable to pass the solution repeatedly through the same peat after adding each time a fresh amount of ammonium nitrate, and in this way it is possible to bring the concentration of the calcium nitrate up to 120 grams per litre without harm to the nitrifying organisms.

The peat may advantageously be replaced by pozzolani or volcanic scoriæ as supports of the nitrification.   W. G.

The Decomposition of Pyruvic Acid by Various Fungi. T. NAGAYAMA (*Biochem. Zeitsch.*, 1921, **116**, 303—306).—Six species of moulds were able to decompose pyruvic acid with production of acetaldehyde. The proportion of the latter was increased by addition of sodium or calcium sulphite.   H. K.

Effect of Salt Proportions and Concentrations on the Growth of *Aspergillus niger*. C. M. HAENSELER (*Amer. J. Bot.*, 1921, **8**, 147—167).—When *Aspergillus niger* is grown on nutrient solutions containing potassium dihydrogen phosphate, calcium nitrate, and magnesium sulphate, increase in the total concentration

of solutions containing the same proportions of salts produces a corresponding increase in yield. The yield is approximately proportional to the amount of nitrate present in the culture, although the partial concentrations of the other two salts can be varied within wide limits without affecting the yields. Calcium nitrate is preferable to sodium nitrate as a source of nitrogen. In cultures with constant proportions of salts and total salt-concentrations, but with sugar-concentrations varying between 1 and 8 atmospheres, the yields of fungus are very nearly proportional to the sugar-concentrations of the cultures.   CHEMICAL ABSTRACTS.

Influence of Temperature on the Utilisation of Dextrose in the Development of *Aspergillus niger*. ÉMILE F. TERROINE and RENÉ WURMSER (*Compt. rend.*, 1921, **173**, 482—483).—For a given medium, the ratio of dry weight of mycelium formed to dextrose consumed in the growth of *Aspergillus niger* is independent of the temperature over the range 22° to 38°.   W. G.

Formation of Vitamin - *A* in Living Plant - tissues. KATHARINE HOPE COWARD and JACK CECIL DRUMMOND (*Biochem. J.*, 1921, **15**, 530—539).—Dried seeds are generally deficient in vitamin-*A*, and, unlike that of the anti-scorbutic vitamin, the amount is not increased on germination. The formation of vitamin-*A* is closely dependent on the presence of chlorophyll; it is formed in green leaves from inorganic salts in water-cultures, but not in etiolated leaves or in mushrooms. Vitamin-*A* is apparently not associated with proteins, but may be removed with fat by solvents, and appears in the unsaponifiable fraction of the latter.   G. B.

The Function of Calcium in the Nutrition of Seedlings. RODNEY H. TRUE (*J. Amer. Soc. Agron.*, 1921, **13**, 91—107).— Seedlings were grown in water culture solutions under laboratory conditions. Injury resulted to plants grown in pure water, for water represents a partial ionic vacuum to roots and tends to establish an equilibrium with cell contents by the withdrawal of ions from the plant. Any one pair of ions will not fully overcome the injurious action, but it is largely overcome by salts yielding the calcium ion; to a less degree it is overcome by those yielding magnesium ions and but slightly or not at all by those carrying potassium or sodium ions. Calcium chloride, carbonate, and nitrate are most abundantly absorbed, whilst calcium sulphate is absorbed by plants which grow on sandy and acid lands. An increase in the number of kinds of nutrient ions present in the solution increases the absorption of electrolytes. Potassium ions when offered in a simple solution are neglected, but when accompanied by calcium ions are absorbed. Calcium ions make potassium physiologically available, whilst a less striking action by potassium ions exists for producing absorption of calcium ions. As the variety of ions present in the solution is increased, the importance of rather sharply marked proportional relations becomes distinctly less than in simpler solutions. The presence of a certain minimal quantity of

calcium ions is probably the most striking single chemical condition of the solution. Doubtless, the physiology of the cell is the basis for an understanding of special services performed by the calcium ion.   CHEMICAL ABSTRACTS.

Effect of Ammonium Sulphate on Plants in Nutrient Solutions supplied with Ferric Phosphate and Ferrous Sulphate as Sources of Iron. LINUS H. JONES and JOHN W. SHIVE (*J. Agric. Res.*, 1921, **21**, 701—728).—Wheat plants grown in the twenty selected Tottingham solutions (cf. *Physiol. Res.*, 1914, [v], **1**, 133) invariably produced a marked decrease in the hydrogen-ion concentrations of the solutions. Plants grown in similar solutions, in which ammonium sulphate was substituted for the potassium nitrate in equivalent osmotic concentrations, invariably caused an increase in the hydrogen-ion concentrations of these solutions during the early stages of growth.

Ferric phosphate, in the quantities used (0·83 mg. of iron per litre), was not sufficiently available in the Tottingham solutions to supply the needs of the plants for iron, but it was readily available to the plants in the solutions containing ammonium sulphate. Ferrous sulphate, used in the same proportion as regards iron, was sufficiently available in the Tottingham solutions to satisfy the needs of the plant for iron. The solutions containing ammonium sulphate with this form of iron in quantities of more than 0·01 mg. of iron per litre were very toxic to the plants, the degree of toxicity increasing with the amount of iron added to the solutions.

The nature of the nutrient solution with respect to the salt constituents and hydrogen-ion concentration appears to determine the availability and the efficiency of a given iron salt for plant growth.   W. G.

Oxalic Acid Content of Young Leaves in Spring Foliage. ARMINIUS BAU (*Zeitsch. techn. Biol.*, 1921, **8**, 151—155; from *Chem. Zentr.*, 1921, iii, 175—176).—The spring foliage of *Sambucus nigra*, *Cratœgus oxyacantha*, *Aesculus hippocastanum*, and barley gave small but measurable amounts of total and water-soluble oxalate. The total oxalate, calculated as oxalate-ion in the dry matter, varied from 0·495% in the young shoots of *Sambucus*, gathered in the afternoon, to 0·03% in the young leaves of barley. The amount of water-soluble oxalate, where estimated, was approximately one-third of the total oxalate. In the case of *Sambucus*, an increase in total oxalate content was observed from early morning to late afternoon.   G. W. R.

The Chemical Constituents of Green Plants. XIII. On the Volatile Basic Substances of Green Plants. HARTWIG FRANZEN, ADOLF WAGNER, and ARTUR SCHNEIDER (*Biochem. Zeitsch.*, 1921, **116**, 208—214).—Out of twenty-eight plants examined all contained volatile basic substances; in the case of thirteen ammonia was identified. The amount of other volatile bases is very minute, even when employing a kilo. of starting material.   H. K.

Significance of "Lignin" Colour Reactions. ERNEST C. CROCKER (*J. Ind. Eng. Chem.*, 1921, **13**, 625—627).—The colour reaction obtained when wood is treated with phloroglucinol, *p*-nitroaniline, etc., is not due to the lignin, but to the traces of an aldehyde which usually, if not always, accompany the lignin; one aldehyde, coniferaldehyde, appears to predominate in wood, vanillin or furfuraldehyde occurring in small quantity only. Certain non-aldehydic substances which are known to yield colour reactions similar to those of " lignin " are shown to contain traces of aldehydes which are responsible for the colour formation. In the case of oil of cloves and oil of sassafras, the aldehyde present appears to be identical with that found in wood. Mäule's reaction (production of a red coloration when wood is treated successively with permanganate, dilute hydrochloric acid, and ammonia) is obtained principally with deciduous woods, and may afford a means of distinguishing these woods from coniferous woods, since the latter yield only a faint brown coloration.　　　　　W. P. S.

Methods of Extracting and Concentrating Vitamins-*A*, -*B*, and -*C*, together with an Apparatus for Reducing Milk, Fruit Juices, and other Fluids to a Powder without Destruction of Vitamins. J. F. McCLENDON (*J. Biol. Chem.*, 1921, **47**, 411—420).—The essential features of the methods are : the use of high pressure in the extraction of vitamin-*A* from dried green leaves or fruit skins moistened with 95% alcohol; the similar extraction, using 80% alcohol, of vitamin-*B* from wheat germ or yeast, followed by the separation of resinous and lipoid material by acidification up to the isoelectric point of these colloids; and the removal of sugar from the vitamin-*B* extract and also from fruit juices containing vitamin-*C* by fermentation with yeast. The extracts so obtained are concentrated by a spray process in which hot flue gases meet a descending spray of the extract. Oxygen is excluded from the flue gases by regulation of the combustion of the furnace.

　　　　　　　　　　　　　　　　　　　E. S.

The Effect of Heat and Oxidation on the Antiscorbutic Vitamin. R. ADAMS DUTCHER, H. M. HARSHAW, and J. S. HALL (*J. Biol. Chem.*, 1921, **47**, 483—488).—The antiscorbutic vitamin in orange juice resists half an hour's boiling at 100° in a reflux apparatus, but is partly destroyed by hydrogen peroxide, especially on warming (cf. Delf, A., 1920, i, 460).　　　　　G. B.

Carrageen (*Chondrus crispus*). II. The Occurrence of Ethereal Sulphates in the Plant. PAUL HAAS (*Biochem. J.*, 1921, **15**, 469—476).—The colloidal hot water extract consists of a substance more soluble in cold water and giving thick, viscous solutions, and one more soluble in hot water, producing solutions which gelatinise on cooling. The latter is the calcium salt of an ethereal sulphate of which the calcium is freely ionised. Sulphate ions cannot be shown to be present until after hydrolysis. This is why the high ash content of carrageen (14·6%) cannot be reduced by dialysis.　　　　　　　　　　　　　G. B.

Manganese in Commonly Grown Legumes. J. S. JONES and D. E. BULLIS (*J. Ind. Eng. Chem.*, 1921, **13**, 524—525).—The following quantities of manganese, expressed as milligrams per kilo of air-dried substance, were found in various leguminous plants :—Vetch, 42; red clover, 33; Alsike clover, 68; lucerne, 23; field peas, 33; sweet clover, 27; white clover, 34. The leaves contained much more manganese than did the other parts of the plants, a fact which supports the theory that the primary function of the manganese is catalytic.   W. P. S.

The Presence of a Glucoside Decomposable by Emulsin in Two Species of *Melampyrum*. MARC BRIDEL and (MLLE) MARIE BRAECKE (*Compt. rend.*, 1921, **173**, 414—416).—*Melampyrum arvense*, L., and *M. pratense*, L., each contain an apparently lævorotatory glucoside which is decomposed by emulsin, giving reducing sugars and a black, insoluble compound. It is suggested that this glucoside may be identical with aucubin, a glucoside found in *Aucuba japonica*, L.   W. G.

The Saponarin in *Mnium cuspidatum*. ANTOINE KOZLOWSKI (*Compt. rend.*, 1921, **173**, 429—431).—The cellular juice of the stem and leaves of *Mnium cuspidatum* contains, in solution, a colourless substance which gives all the reactions of saponarin. Its presence could not, however, be detected in other species of *Mnium* or in other mosses.   W. G.

The Chemical Composition of Peanut Oil. GEORGE S. JAMIESON, WALTER F. BAUGHMAN, and DIRK H. BRAUNS (*J. Amer. Chem. Soc.*, 1921, **43**, 1372—1381).—Two samples of peanut oil were examined, but in neither case was there any indication of the presence of hypogæic acid. The compositions of the two samples were :—unsaponifiable matter 0·2, 0·3%; glycerides of oleic acid, 52·9, 60·6%; of linolic acid, 24·7, 21·6%; of palmitic acid, 8·2, 6·3%; of stearic acid, 6·2, 4·9%; of arachidic acid, 4·0, 3·3%, and of lignoceric acid, 3·1, 2·6% respectively.   W. G.

Constituents of *Pelvetia Wrightii*, Yendo. KINSUKE KONDÔ (*J. Chem. Soc. Japan*, 1921, **42**, 537—545; cf. this vol., i, 387).
                    K. K.

The Cellulose Content of Spruce Wood. P. KLASON (*Svensk Pappers Tidning*, 1921, **24**, 7; cf. A., 1920, i, 148).—By continuing the digestion of spruce wood for ten to twenty days, the following revised analytical results were obtained : cellulose free from pentosans, 53%; hemicellulose, 15%; lignin, 30%; other substances, 2%.   CHEMICAL ABSTRACTS.

General and Physical Chemistry.

The Luminosity of Mercury Vapour Distilled from the Arc in a Vacuum. NORMAN H. RICKER (*Physical Rev.*, 1921, **17**, 195—226).—Considerable evidence is offered in support of Child's contention (*Phil. Mag.*, 1913, [vi], **26**, 906) that the afterglow in mercury distilled from an arc is due to a recombination of positive and negative ions. Strutt's work (*Proc. Roy. Soc.*, 1918, **94**, [*A*], 88) was repeated and confirmed and it is shown to be not inconsistent with Child's conclusion (cf. *Phil. Mag.*, 1919, [vi], **37**, 61). The author obtained enhanced luminosity by heating the mercury thode. The luminous vapour passed through a hollow nickel ode into a heated tube containing two or more grids. On charg-g one of the grids positively, a current flow as great as 1 ampere 5 volts could be obtained. The red glow which first filled the be diminished on both sides of the grid up to a grid voltage of after which it was replaced by a blue glow. The change in our was found to be caused merely by a relative change in tensity of certain lines in the mercury spectrum. On charging grid negatively, the luminosity upstream is not diminished even 300 volts and downstream but slightly. The current is a small art of an ampere and never reaches saturation; so that quenching far from complete. A jet of mercury vapour sent into the minous stream serves merely to dilute the light. The vapour elocity was determined by applying a high-frequency voltage to ne grid with a stroboscopic wheel so that the luminosity appeared puffs which could be accurately observed. The velocity was 740 cm. per sec. Then from the rate of distillation the vapour ensity was calculated and shown to be essentially constant along he tube. The rate of decay of luminosity was observed with a utting polarisation photometer and compared with formulæ erived on three assumptions: (1) that the positive ions emit light pontaneously and not continuously; (2) that the light is produced uring recombination of positive and negative ions, and (3) that ight is continuously emitted by positive ions. Formula 2 fitted he observed decay better than 1, each having but one arbitrary constant; but formula 3 with two arbitrary constants would fit almost any set of data; so it is impossible to decide in its case. All the facts observed support Child's claim that the light is caused by recombination of ions. CHEMICAL ABSTRACTS.

Vacuum Spark Spectra in the Extreme Ultra-violet of Carbon, Iron, and Nickel. R. A. MILLIKAN, I. S. BOWEN, and R. A. SAWYER (*Astrophys. J.*, 1921, **53**, 150—160; cf. this vol., ii, 3, 363).—By using a specially ruled grating containing 500 to 1100 lines per mm., the intensities and wave-lengths ($\pm 0 \cdot 2$ Å.) of 75 lines due to carbon (λ 360—λ 1931), of 200 lines due to iron (λ 271—λ 2153), and of 75 lines due to nickel (λ 731—λ 1860) have been measured. CHEMICAL ABSTRACTS.

Intensity Differences in Furnace and Arc among the Component Series in Band Spectra. ARTHUR S. KING (*Astrophys. J.*, 1921, **53**, 161—164).—Under high dispersion, the A_1 series of lines in the cyanogen band at λ 3883 is enhanced over the A_2 series in the furnace as compared with their behaviour in the arc. Some new doublets appeared in the furnace. The two series appear to belong to different temperature classes and may be expected to differ in other characteristics. The cyanogen band at λ 4216 showed similar differences between furnace and arc. In the Swan band at λ 5165 the triplet series is enhanced in the furnace spectrum with reference to the adjacent doublet series. The bearing of these data on atomic structure is pointed out.   CHEMICAL ABSTRACTS.

Obliteration of the Characteristic Spectra of Metals by certain Gases. GEORGE E. GIBSON and W. ALBERT NOYES jun. (*J. Amer. Chem. Soc.*, 1921, **43**, 1255—1261).—When sodium chloride is melted below a spark gap in oxygen and sparks are passed they are brilliant yellow in colour and show the D line distinctly, but if the oxygen is displaced by chlorine the spark becomes pale blue and only the merest trace of the D line can be observed, and it is further noticed that the spark passes with great difficulty. Similar experiments were made with a number of gases using sodium, thallium. and mercury salts and it was found that of thirty-seven gases and vapours examined twenty-three obliterated the characteristic lines of the salts used. An approximate measure of the sparking potential was also obtained by placing a parallel spark gap outside the apparatus and varying this until the spark just failed to pass across it. Vapours of carbon disulphide, sulphur, carbon tetrachloride, sulphur dichloride, arsenic, iodine, stannic chloride, bromine, chlorine, nitrogen dioxide, boron trichloride, phosphorus trichloride, arsenic trichloride, silicon tetrachloride, titanium tetrachloride, arsenious oxide, sulphur trioxide, acetylene, sulphur dioxide, selenium, phosphorus, hydrogen iodide, and ferric chloride obliterate the characteristic spectrum, whilst nitric oxide, carbon monoxide, hydrogen sulphide, oxygen, nitrogen. hydrogen, carbon dioxide, ammonia, mercury, hydrogen chloride. hydrogen bromide, thallous chloride, and mercuric chloride do not affect the spectrum. The gases which exert the obliterating power have also a high sparking potential, and in the main are the gases which, on Lewis's theory of molecular structure, are to be expected to have the power of combining readily with electrons or to dissociate in the spark into gases of this character. The parallelism between high sparking potential and power to obliterate the spectrum lines is explained on the assumption that the molecules of gases which have these two properties unite with free electrons to form ions of larger mass which are incapable of producing further ionisation.   J. F. S.

Induction Spectrum of Rubidium. LOUIS DUNOYER (*Compt. rend.*, 1921, **173**, 472—474).—Using the method previously applied to cæsium (this vol., ii, 529), the author has obtained an induction spectrum of rubidium showing 332 lines between $\lambda = 2294$ and

λ=5525. The principal rays and their intensities are tabulated in the original. Most of the intense rays have been found in the spark spectrum by Exner and Haschek, but some of the rays of the spark spectrum do not appear in the induction spectrum.

W. G.

The Rôle of Electrical Actions in the Emission and Appearance of certain Types of Rays in the Spectrum of Magnesium. A. DE GRAMONT and G. A. HEMSALECH (*Compt. rend.*, 1921, **173**, 505—511).—The authors have extended their work on the appearance of spark rays of lead and tin in the electric arc (cf. *ibid.*, 1921, **173**, 278) to the case of magnesium. Details are given of the variation in the lines produced by changing the conditions under which the spark or arc is maintained. The arc was struck between magnesium electrodes under glycerol, petroleum, and water, and sparks were passed in hydrogen, oxygen, coal gas, and nitrogen. The emission of spark rays by the arc, under liquid layers, is independent of the nature and conductivity of the liquid. The emission of these rays is apparently regulated by electrical forces, and their sudden cessation corresponds with a certain critical value of the electrical forces below which their emission cannot be sustained. The remarkable symmetrical broadening of the spark ray, as well as the broadening towards the red of the rays of the Rydberg series during the first phase of the arc, is a manifestation of the Stark effect.

W. G.

Fine Structure of Band Spectra. E. GEHRCKE and L. C. GLASER (*Ann. Physik.*, 1921, [iv], **65**, 605—608).—The structure of the band spectra of magnesium, mercury, and carbon has been investigated. As source of light, the arcs of the substances in a vacuum were used. The light from the arc fell on a plate parallel plate 5 mm. thick, and the interference bands, in the same manner as employed by Galli and Förstling (*Physikal. Zeitsch.*, 1917, **18**, 155) were projected on the slit of a prism spectrograph. In the case of magnesium, the lines $\lambda\lambda$ 5529 and 4703 were seen very sharply whilst $\lambda\lambda$ 5184, 5173, 5167, and 4352 and the green triplet were found, but these were less sharp. Mercury showed the lines $\lambda\lambda$ 4358, 4348, 4340, 4078, 4047, and three extended series of lines with the limiting line at $\lambda\lambda$ 4396, 4218, and 4017 respectively. Carbon shows the heads of the bands much less sharply than the preceding cases. Interference is, however, shown by the heads of the carbon bands, particularly at $\lambda\lambda$ 4216 and 4197. The distance between two interference maxima corresponds with 0·16 Å.U. in the blue and 0·15 Å.U. in the violet.

J. F. S.

Spectra of Lead Isotopes. T. R. MERTON (*Proc. Roy. Soc.*, 1921, [A], **100**, 84—88).—Comparative measurements of the wavelength of the line 4058 Å.U. with ordinary lead and lead from carnotite showed a difference of 0·011±0·0008 A.U. The difference is about two hundred times that expected on Bohr's theory if the

difference is calculated in the same manner as that between the Balmer lines of hydrogen and the enhanced helium lines.   J. R. P.

The Variation with Temperature of the Electric-furnace Spectrum of Manganese. ARTHUR S. KING (*Astrophys. J.,* 1921, **53**, 133—143).—The spectrum produced in the tube resistance furnace at 1700°, 2000°, and 2400° was examined from λ 2795 to λ 8200, but no lines were found beyond λ 6500. The relative intensities of the lines in the arc spectrum and in the furnace spectra at the different temperatures are tabulated, and the temperature classification of the lines is given. Some lines were observed at 1560°; the triplet λ 4031 to 4035 was strong and well reversed at this temperature. As with other furnace spectra, the ultra-violet wave-length limit is shorter the higher the temperature. None of Lockyer's enhanced lines occurs in the furnace. The behaviour of various types of lines is given in detail. Of special interest is the triplet at λ 2800, which is always reversed, and the one at λ 4033 the intensity of which depends on the quantity of vapour present.   CHEMICAL ABSTRACTS.

Symmetrical Coupled Groups of Lines in the Iron Spectrum. E. GEHRCKE (*Ann. Physik,* 1921, **65**, 640—642).— A theoretical paper in which the author describes a number of regularities in the violet end of the iron spectrum which are visible in the photographs recently published by Glaser (*Ann. Gewerbe u. Bauwesen,* 1921, **88**, 32). It is shown that six groups of lines exist which both with regard to position and intensity of the components are symmetrical about a middle point. These are a group of six lines, with its centre at λ 4221 Å.U., a group of fourteen lines with the centre at λ 4215, a group of six lines with the centre at λ 4193·3, a group of ten lines with the centre at 4195·5, a group of nine lines with the centre at λ 4235, and a group of sixteen lines with the centre at λ 4199·3. These groups are not quite independent of one another, for it is shown that the two extreme components of the first-named group and the left inner component also belong to the second group. Similar coupled symmetrical groups have also been observed in the spectra of tungsten and molybdenum. It is suggested that a Zeeman effect or a Stark effect on account of the magnetic or electric field of the atom itself is responsible for the regularity, which is explicable if one of the twenty-six electrons on the surface of the atom changed its position due to the action of the field.   J. F. S.

Influence of Elevated Temperature on the Fluorescence and Absorption Spectra of Iodine Vapour of Constant Density. J. PRINGSHEIM (*Zeitsch. Physik.,* 1921, **5**, 130—138).—The influence of elevated temperatures on the fluorescence and absorption spectra of iodine vapour has been examined. It is shown that whilst the colour change from green to yellow which occurs in the fluorescence of iodine vapour by raising the vapour density is due to an increased absorption in the short wave-length region of the band spectrum the superficially quite similar change which is observed by simply

raising the temperature is brought about by a decreased primary absorption and consequent reduced fluorescence in the corresponding spectrum region. The heating of iodine vapour at a constant density brings about, not only a displacement of the intensity in the whole absorption spectrum, but also effects an extensive change in the partition of energy of the individual bands.

J. F. S.

Ultra-red Absorption Spectra of Solid Substances in Thin Layers. O. REINKOBER (*Zeitsch. Physik.*, 1921, **5**, 192—197).— The ultra-red absorption spectra of the ammonium haloids have been measured. The method of preparing transparent layers for examination consisted in subliming the substances on to thin plates of transparent material, such as quartz, fluorspar, and rock salt. The spectra have been measured up to wave-lengths of about 8μ. The method is superior to the reflection method, particularly in the greater clearness of the spectra obtained. The following characteristic frequencies have been observed: ammonium fluoride 3·5, 4·5, 5·0, 6·0 ?, and 6·69μ; ammonium chloride, 3·24, 3·5, 4·25, 4·95, 5·66, and 7·07μ; ammonium bromide, 3·22, 4·3, 4·9, 5·9, and 7·10μ; ammonium iodide, 3·22, 4·27, 5·0 ?, 6·0 ?, and 7·15μ. These values are claimed to be more accurate than the corresponding values found by the reflection method, and they contain twelve values not found by that method. J. F. S.

Absorption Spectrum of Oxygen. J. DUCLAUX and P. JEANTET (*Compt. rend.*, 1921, **173**, 581—583).—Using a water prism, the authors have studied the ultra-violet absorption spectrum of oxygen, between $\lambda=1900$ and 2000. In addition to the seven bands observed by Bloch between $\lambda=1830$ and 1960, they find an eighth belonging to the same group which corresponds with the frequency formula $N=50727-2\cdot8m^2$, where $m=1$ to 9. A ninth band was observed but exact measurements were not made. A second group of bands similar to, but much weaker than, the first was observed in this region. The second group may be deduced from the first by a simple translation in the frequency scale, there being a difference of 1555 in the frequencies of corresponding rays in the two groups. W. G.

The Calculation of the Colour of " Cyclic " Coloured Substances. JAMES MOIR (T., 1921, **119**, 1654—1668).

The Numerical Values of the Optical Rotations in the Sugar Acids. P. A. LEVENE (*J. Biol. Chem.*, 1921, **48**, 197—202).—A theoretical paper in which calculations are made, by Hudson's method, of the optical rotations of the different asymmetric carbon atoms in the hexosamic acids. Using different combinations of four equations, it is shown that constant values for the β, γ, and δ carbon atoms are obtained only when the combination is so chosen that the value for the α-carbon atom is the same for each member of the combination. The author concludes that the superposition theory holds only within certain limits. E. S.

The Inversion of the Rotatory Power of Derivatives of Tartaric Acid. D. DE MALLEMANN (*Compt. rend.*, 1921, **173**, 474—477; cf. this vol., i, 158).—Sodium hydrogen *d*-tartrate shows a diminution in its rotatory power when dissolved in a saturated solution of sodium chloride and an inversion when dissolved in a strong solution of calcium chloride. Similarly, calcium *d*-tartrate shows a slight lævorotation when dissolved in calcium chloride solution. Ethyl *d*-tartrate has its rotatory power inverted in the presence of calcium chloride in either aqueous or alcoholic solution. Contrary to the effect of calcium chloride, the presence of copper chloride results in an increase in the rotatory powers of both *d*-tartaric and *d*-malic acids, both acids becoming more dextro-rotatory.   W. G.

Photochemical Decomposition of Silver Bromide. I. ROBERT SCHWARZ and HEINRICH STOCK (*Ber.*, 1921, **54**, [*B*], 2111—2122).—Owing to the non-availability of a suitable source of artificial light, the experiments deal with the behaviour of silver bromide towards daylight the intensity of which is measured by a self-recording actinometer. The silver bromide is prepared by the slow addition of potassium bromide solution (10%) in moderate excess to a dilute solution of silver nitrate acidified with nitric acid, the solutions being gently mixed; the preparations are effected in red light. The silver bromide is used in three forms, (*a*) a caseous, flaky modification prepared as described, which passes when preserved into the plastic variety (*b*), and (*c*) the pulverulent modification obtained by shaking (*b*) with water. The silver bromide is allowed to settle on the bottom of small crystallising dishes in the form of a thin, uniform film and is washed repeatedly with water until free from bromide ions. It is covered with water and exposed to light in an apparatus which is so arranged that a current of air carries the liberated bromine into an aqueous solution of potassium iodide. According to the intensity of the illumination, the production of bromine is noticeable at the end of five to fifteen minutes. The experiments were generally continued for about four hours, at the end of which the bromide had assumed a pale grey to brown colour; variety (*a*) retains its caseous consistency, whereas the more compact form (*b*) suffers a further contraction and sometimes becomes detached from the edges, whilst form (*c*) remains unchanged except with regard to colour. The elimination of bromine occurs with the same regularities as are observed in the blackening of photographic emulsions. The sensitiveness of the various forms towards light diminishes in the order *b—a—c*. The time which is allowed for the transformation of form *a* into *b* is a matter of considerable importance, since the sensitiveness again diminishes when the form is more than one hundred and ten hours old. The most sensitive products are obtained after eighty to ninety hours. It is probable that a gradual change of form *b* into the less sensitive variety *c* occurs when agitation is avoided. Solarisation is a property of pure silver bromide, and is accompanied by diminished elimination of bromine. Speci-

mens of silver bromide obtained by the action of an excess of silver nitrate on potassium bromide do not evolve bromine when illuminated, but yield, in its place, a volatile substance which oxidises iodine. The phenomenon is explained on the hypothesis that the precipitate adsorbs silver nitrate and that fission of the silver bromide into silver and bromine actually occurs; the latter reacts with the adsorbed silver nitrate with the formation of hypobromous acid; the latter is removed by the air and oxidises the iodine in accordance with the equation : $I_2 + 5HBrO + H_2O = 2HIO_3 + 5HBr$. The constancy in weight which has been observed in silver bromide when prepared in this manner and subjected to illumination is attributed to the re-formation of silver bromide from hypobromous acid and the liberated silver. Pre-illumination of silver bromide (by cautious exposure to light during precipitation) causes a greatly increased liberation of bromine on subsequent exposure.   H. W.

The **Developing Properties of Leuco-bases of Dyes derived from Rosaniline.** A. LUMIÈRE, L. LUMIÈRE, and A. SEYEWETZ (*Bull. Soc. chim.*, 1921, [iv], **29**, 829—833).—The authors, working with pure substances, were unable to repeat Abribart's results (cf. *ibid.*, 1921, [iv], **29**, 265) on the use of the leuco-bases of malachite green and rosaniline as developers. They consider that his results were probably due to impurities in his leuco-bases.   W. G.

The **Corpuscular Spectra of the Elements.** MAURICE DE BROGLIE and LOUIS DE BROGLIE (*Compt. rend.*, 1921, **173**, 527—529).—A discussion of the results obtained in the corpuscular excitation by X-rays of the heavy metals, uranium, lead, and thorium. The bearing on the L, M, and N layers of electrons is considered.   W. G.

Fine Structure of Röntgen Spectra. II. L Series. ADOLF SMEKAL (*Zeitsch. Physik.*, 1921, **5**, 91—105; cf. this vol., ii, 292).— It is shown that the whole of the Röntgen lines attributed to the L spectrum of tungsten can be brought into one general scheme, which demands the existence of at least five M layers. The existence of these is rendered fairly certain by a pair of well-defined lines in each case. This reasoning shows the necessity of the determination of the quantum condition of each electron sheath by means of three quantum numbers. The explanation of K_β offered by Kossel (*ibid.*, 1920, i, 119) is confirmed and explanations are given for all hitherto uninterpreted K and L lines, which are in keeping with the relationships as found in the case of tungsten. The new relationships $K_\beta - K_{\beta'} = L_\psi - L_\nu$ and $K_\beta - K_\alpha = L_\delta + L_1 - L_3$ have been tested and found to be in complete accord with the known experimental data within the limits of experimental error.
                                                        J. F. S.

Fine Structure of Röntgen Spectra. III. M Series and the Principle of Selection. ADOLF SMEKAL (*Zeitsch. Physik.*, 1921, **5**, 121—129; cf. this vol., ii, 292, and preceding abstract).— A paper supplementary to two previous papers (*loc. cit.*) in which

definite frequency relationships are given for the M lines γ and δ, and in the case of the other uninterpreted M lines the most probable of the possible explanations is pointed out. The relationship $M_\gamma = L_3 - L_1 - (L_\phi - L_\gamma)$ is the only relationship giving complete agreement with facts, which can be found from the investigation of a great range of order numbers. It is shown how apparent difficulties in the principle of selection, as in the case of Kossel's arrangement of K_β, may be avoided. On the other hand, on account of a lack of exact relative intensity data for the whole of the lines, it is not possible to draw general conclusions as to the form of the principle of selection which holds for energy levels which are unlike hydrogen. J. F. S.

Action of Infra-red Rays on Phosphorescence. MAURICE CURIE (*Compt. rend.*, 1921, **173**, 554—555; cf. this vol., ii, 233).— No diminution was noticed in the intensity of the radiation reflected from the face 110 of a cubic crystal of blende illuminated by X-rays after inundating the crystal with infra-red rays. W. G.

The Opening up of Earths Poor in Radium. ERICH EBLER and A. J. VAN RHYN (*Zeitsch. angew. Chem.*, 1921, **34**, 477—480; cf. Ebler and Bender, A., 1915, ii, 128).—A number of uranium minerals, including carnotite and the uranium micas autunite and chalcolite, which are found in a magma of sandstone or decomposed granite, have been examined with the object of discovering a simple method of extracting the radioactive elements from the bulk of the inactive material. In the case of Portuguese uranium micas, more than forty times as much radium was found in the micaceous material, separated mechanically from the ground-mass of siliceous material, as in the latter, but the proportion of radium to uranium in the mica, $1\cdot7 \times 10^{-7}$, was less than in the ground-mass, $9\cdot8 \times 10^{-7}$, the latter being greater than the theoretical value, $3\cdot4 \times 10^{-7}$. This anomaly may be explained on the assumption that part of the radium has been dissolved out of the mica by infiltration, and then partly redeposited in the absorbent siliceous mass, consisting of decomposed granite and containing as much as $94\cdot2\%$ of SiO_2. Experiments with normal granite show that over 60% of the radium present is contained in the mica and hornblende, the rest in the felspar, whilst the quartz is free from radium.

More than 80% of the radium present in these minerals can be obtained in the form of crude sulphate by the following method. The powdered mineral is mixed with about an equal weight of sodium or calcium chloride and calcium carbonate, and heated at the sintering temperature (800—$1000°$) for five or six hours in a muffle furnace. The cooled mass is powdered and extracted with dilute hydrochloric acid containing sulphuric acid and barium chloride. The sulphate precipitate containing the radioactive material can then be readily washed away from the coarse inactive particles and filtered off. The weight of crude sulphates obtained is about 7% of the original ore. This method was used to extract radium from Portuguese torbernite ore containing only $4\cdot5 \times 10^{-7}\%$

rom Colorado carnotite sandstone containing $5.0 \times 10^{-7}\%$ and from Mexican pitchblende-quartzite containing $2.84 \times 10^{-7}\%$ of radium.

<div align="right">E. H. R.</div>

The **Disintegration Constant of Radium Emanation.** W. BOTHE and G. LECHNER (*Zeitsch. Physik.*, 1921, **5**, 335—340).— The disintegration constant of radium emanation has been determined by comparing the emanation directly with the radium preparation from which the standard solution was made. Two values of λ were obtained which agreed to one per thousand, and have a mean of 0.1819 day$^{-1}=2.106 \times 10^{-6}$ sec.$^{-1}$. From this the half life is 3.810 days. These values are about 1% greater than the generally accepted Curie-Rutherford values. It is shown that in emanation measurements the often untrustworthy standard solution can be dispensed with if a radium standard and some radium emanation are available. The once determined sensitiveness of the emanation electrometer, found by means of a tube of emanation, may be made the basis of measurements for a long time, if the γ-ray sensitiveness is controlled for each measurement. A table is appended to the paper which gives the decay of radium emanation and the formation in radium preparations which are not in equilibrium.

<div align="right">J. F. S.</div>

Range and Ionisation of the α-Particles from Radium-C and Thorium-C. G. H. HENDERSON (*Phil. Mag.*, 1921, [vi], **42**, 538—551).—The ionisation curves of Ra-C, Th-C_1 and Th-C_2 in air were measured, particular attention being directed to the end portions. A considerable part of each curve is approximately a straight line. The gradual flattening of the curve at the end of the range can be accounted for by small variations in the ranges of individual α-particles, due to probability variation in the number of electrons encountered by the α-particle along its path. An "extrapolated range" is suggested as more suitable than the usual definition, and is obtained by prolonging the straight part of the curve. This extrapolated range in air at $0°$ is 6.592 cm. for Ra-C, 3.529 cm. for Th-C_1, and 8.167 cm. for Th-C_2. A general equation for the end part of the curve is suggested.   J. R. P.

The **Accumulation of Radioactive Substance in Ferruginous Spring Deposits.** F. HENRICH (*Ber.*, 1921, **54**, [*B*], 1715—1722). The preliminary treatment of the sediment is effected with hydrochloric acid, whereby a portion remains undissolved which contains silica (46.7%), calcium oxide (12.1%), iron oxide (11.5%), aluminium oxide (4.44%) organic matter (3%), and smaller amounts of arsenic, manganese, etc. The solution is treated with ammonia, giving a precipitate containing iron oxide (61%), calcium oxide (5.8%), manganese oxide (5.7%), aluminium oxide (3.67%), and small amounts of arsenic, strontium, etc., together with 2.54% of matter insoluble in hydrochloric acid. The latter is re-dissolved, but enrichment of the solution in radioactive matter is found impossible by fractional precipitation of the iron as ferric hydroxide. If, however, the iron is reduced to the ferrous state and slow

<div align="right">23*</div>

crystallisation of ferrous sulphate is induced, it is found that the initial deposits are completely inactive and the subsequent ones only slightly active, becoming, in general, completely inactive after a single crystallisation from water. A very considerable enrichment of the solution can thus be effected, and the active material can then be deposited on ferric hydroxide by oxidation and subsequent addition of ammonia to the solution. If desired, the last traces of iron can be removed electrolytically from the solution and the active substance then deposited on any desired carrier, but the procedure does not appear to offer any particular advantage.

The residue (see above) is treated with hydrofluoric and sulphuric acids for the removal of silica, whereby the organic matter becomes charred and the carbon disseminated through the inorganic matrix. The latter may be almost completely removed by treatment with boiling hydrochloric acid $(1:2)$. The residue invariably exhibits relatively great activity, which is yet more pronounced in the ash left after ignition. Attempts to secure an active deposit by treatment of the solutions with animal charcoal were, however, unsuccessful. The filtrate from the treatment of the charred product is concentrated when gypsum and alum successively separate in an inactive condition; subsequent concentration of the active matter is then effected by the ferrous sulphate method.   H. W.

Further Light on the Theory of the Conductivity of Solutions. GUY CLINTON (Pamphlet, pp. 15).—A theoretical discussion of the hypothesis of electrical conduction of solutions. It is pointed out that Kohlrausch's principle is stated first as a law of moving ions and secondly as a function of the resistance. The illustration put forward by Hittorf is examined, and shown to be incapable of showing the possibility of the equivalency of discharge when the ions move with unequal velocity. The same question is examined mathematically, and the conclusion is drawn that Kohlrausch's law of ionic movements is not in harmony with Faraday's law of discharge. It is suggested that the Kohlrausch statements need revision, to keep them within the limit of experimental evidence. The author proposes the following: During the early period of electrolysis, in parts of the cell remote from the points of discharge, with certain amendatory assumptions, the sum of the velocities of the kation and anion is proportional to the molecular conductivity of the solution. It is pointed out that velocities have been measured in but a small part of the cell, whilst resistance is measured for the whole cell, and that such values are not comparable. The author describes a cell in which the velocity for the whole distance between the electrodes is determined. This, only, is comparable with the fall in the potential for the entire cell. It is shown experimentally that the lead ion moves downward toward the cathode with a velocity of 0.113 cm. per sec., but upward to the cathode with a velocity 0.00457 cm. per sec, the potential gradient being unity in each case. Whetham's explanation for the exceptional congestion in solutions of cadmium iodide is quoted, and it is suggested that it might be applied to explain all cases of

congestion. The effect of hydration of ions on ionic velocities is examined. It is pointed out that previous work takes no account of the eddies formed in the system.　　　　　　　　　　J. F. S.

Ionic Mobilities, Ionic Conductivities, and the Effect of Viscosity on the Conductivity of certain Salts. DUNCAN A. MacINNES (*J. Amer. Chem. Soc.*, 1921, **43**, 1217—1226).—A theoretical paper in which it is shown that the changes in the transport numbers with concentration indicate that variations of ionic mobility with concentration must be considered in any theory of strong electrolytes. Since the changes in the transport numbers can indicate only differences of mobilities, it seems very probable that the actual changes are greater than these differences. Since there is at present no method of distinguishing between variations of the equivalent conductivity due to (*a*) changes of the number of ions, (*b*) changes of the mobilities of the ions, it seems desirable to consider a group of these substances as completely dissociated, and all variations of conductivity as due to changes of mobility. The latter changes can conceivably arise from the increasing strength with concentration of the electrical field due to the ions. The evidence in favour of this view is most clear in the case of the alkali haloids and hydrochloric and nitric acids. These substances fulfil a further condition of complete dissociation, namely, additivity at each concentration, of the conductivity except in so far as this property is modified by the changing viscosity. Any degree of dissociation less than that represented by the limiting case can be found in solutions of electrolytes, particularly of weak electrolytes and those possessing multivalent ions. But this dissociation cannot be calculated from the ratio Λ/Λ_0, since the changes of the transport numbers with concentration indicate that changes of ionic mobility also occur in these solutions. In the case of strong electrolytes, there does not appear to be any property which can be computed from the conductivity ratio. The activity coefficients of the ions of the alkali chlorides and hydrochloric acid are first lower and then much higher than the corresponding ratios as the concentrations are increased, whilst the free energy contents of these ions have been found to be additive at each concentration, as would be expected if they were completely or almost completely dissociated.　　　　　　　　　　J. F. S.

Electrode Reactions. Contractometric Observations at Anodes. V. KOHLSCHÜTTER and H. STÄGER (*Helv. Chim. Acta*, 1921, **4**, 821—837).—An extension of the contractometric method (A., 1920, ii, 728) to the study of anode changes in electrolytically unchangeable electrolytes, yielding hydrogen at a platinum black electrode. The anodes consisted of electrolytic deposits of the metal to be investigated on platinum contractometer plates, a sheet of the metal itself being alternatively employed in the case of copper (cf. A., 1920, ii, 624). The results of a study of platinum anodes in sulphuric acid or sodium hydroxide solution, of nickel, copper, and iron anodes in sodium hydroxide solutions, of passive iron in nitric acid, and of copper and silver in sodium sulphide

solutions show that the method is not inferior in applicability to the dilatometric method. The details do not lend themselves to concise reproduction.   J. K.

Electrode Processes in the Presence of Colloids. N. ISGARISCHEV (*Koll. Chem. Beihefte*, 1921, **14**, 25—62).—The cathodic and anodic polarisation in the electrolysis of solutions of zinc sulphate and copper sulphate has been investigated in the presence of gelatin, gum, and sucrose. The potential of zinc and copper has been determined in the same solutions and also the viscosity and the electrical conductivity of the solutions. It is shown that a maximum polarisation is set up and also a maximum potential at a definite concentration of the added substance. In a molecular solution of zinc sulphate the maximum occurs with 0·025% of gelatin, 2% of gum arabic, and 30% of sucrose, and with copper sulphate solution the maximum occurs with 0·30% of gelatin. This maximum is explained by the hypothesis that the kations form adsorption compounds with the colloid and these exert an action on the velocity of the cathode processes, but none on the anode processes. In the case of sucrose, the polarisation is explained as due to a chemical combination between the sugar and the zinc sulphate. The heat of formation of the adsorption compound between the zinc ion and gelatin is found by the electrometric method to be $\Delta Q = -2150$ Cal. The ultra-microscopic investigation of the above-named solutions shows a characteristic change in the form of the particles with increasing colloid concentration. A connexion between the polarisation phenomena and the structure of the electrolytically deposited metals is established. The change in the crystallisation phenomena, the crystalline form of the metal, and the polarisation are brought about by the relatively slow formation of the ions from the complexes. Similar results have also been obtained with solutions of nickel sulphate. In this case the maximum polarisation is found with solutions containing 0·95% of gelatin.   J. F. S.

Electrolytic Oxidation and Reduction in Presence of Metallic Salts. MAX SCHLÖTTER (*Zeitsch. Elektrochem.*, 1921, **27**, 394—402).—In the electrolysis of chloride solutions for the manufacture of chlorate, the addition of a small quantity of a metallic salt, for instance a manganese salt or a chromate, has a favourable effect on the current efficiency of the process, apparently by preventing reduction from taking place in the cell. Experiments to investigate the part played by the metallic salt were made, using as electrolyte a saturated solution of potassium chloride with platinum electrodes. The amounts of reduction and of decomposition of water taking place were determined by analysis of the electrode gases for hydrogen and oxygen. It was found that the effect of the addition of a metallic salt to the electrolyte was determined, not only by the character of the metal, but equally by its concentration. Certain metals, such as copper (0·5 gram of cupric chloride per litre) and lead (0·21 gram lead dioxide per litre), eliminated reduction almost entirely. Tin, when 0·5

gram of stannous chloride per litre was added, had little effect, but when only one-tenth of this quantity was used, reduction was brought down to a very low figure. It was always observed that, after addition of the metal salt, several hours had to elapse before the cell settled down to a steady state. This is probably due to the time required for the deposition of the metal on the electrode. Since the most favourable results are obtained with a very small quantity of added metal, it appears that the cathode does not then become completely covered with the deposited metal, but that the latter forms a network over the electrode metal. The form of electrode which then gives the best results is probably one which consists of the system electrode metal–deposited metal–hydrogen. This conclusion was supported by experiments in which metals other than platinum were used for the cathode. When a copper cathode is used, addition of copper to the electrolyte has no effect on the reduction. With an iron electrode addition of copper increases the amount of reduction in the cell, whilst with a copper electrode addition of iron lowers the percentage reduction, although the reduction value of a pure iron electrode is much higher than that of a pure copper electrode. This is explained by the fact that electrolytically deposited iron absorbs more than one hundred times its volume of hydrogen, forming a stable system in which the activity of the hydrogen is reduced to a low value. The potential energy of the hydrogen at the cathode depends on the nature of the deposited metal, and it should be possible, by choosing a suitable system, to obtain conditions for the quantitative reduction of any substance.   E. H. R.

Velocity of Sound in Gases at High Temperatures and the Ratio of the Specific Heats. HAROLD B. DIXON, COLIN CAMPBELL, and A. PARKER (*Proc. Roy. Soc.*, 1921, [*A*], **103**, 1—26).— Direct measurements were made of the time taken by a sound wave to travel through the gas contained in a tube of known length, by means of a pendulum chronograph. The sound was propagated through tubes of lead, mild steel, and silica. The lead tubes were used up to 100°; at higher temperatures, the steel and silica tubes were used, being heated in a gas furnace, and electrically, respectively. The values of c_p/c_v and the true specific heats calculated by Berthelot's equation, are given : for air (0—700°), nitrogen (0—1000°), carbon dioxide (0—600°), methane (0—600°), and ethane (0—100°), and the values of c_v are represented by the following equations (t=temperature ; T=absolute temperature) : nitrogen $4\cdot775+0\cdot00042T$; air $4\cdot8+0\cdot0004T$; carbon dioxide $6\cdot30+0\cdot02205T+0\cdot0000007T^2$; methane $6\cdot66+0\cdot019t$; ethane $9\cdot04+0\cdot0183t$.   J. R. P.

Ratio of the Specific Heats of Air and Carbon Dioxide. J. R. PARTINGTON (*Proc. Roy. Soc.*, 1921, [*A*], **100**, 27—49).—The values of c_p/c_v for air and carbon dioxide at 17° were found by the method of adiabatic expansion and the specific heats calculated by Berthelot's equation. For air, $c_p/c_v=1\cdot4034$; for carbon dioxide, $c_p/c_v=1\cdot3022$.   J. R. P.

Freezing Points of Organic Substances. VI. New Ex-perimental Determinations. J. TIMMERMANS and TH. J. F. MATTAAR (*Bull. Soc. chim. Belg.*, 1921, **30**, 213—219; cf. A., 1911, ii, 854; 1914, ii, 168; this vol., ii, 430—431).—The freezing points of seventy-three compounds of the fatty series, liquid at the ordinary temperature, including alkyl haloids, ethers, ketones, acid anhydrides and chlorides, esters, and amines, are given in tabulated form with notes and references to earlier determinations where such have been made. The freezing points given range from $-13°$ to $-140°$.

J. H. L.

Some Relations between Absolute Critical Temperatures of Ebullition and Fusion. J. J. VAN LAAR (*J. Chim. physique*, 1921, **19**, 4—8).—The regularities described by Prud'homme (A., 1920, ii, 587) are purely arithmetical and have no physical meaning. Relations are deduced from the formula of van der Waals: $\log p/p_c = f(T_c/T - 1)$, where f may depend slightly on temperature. If $T_1 =$ boiling point, $p = 1$ atm., then $\phi_1 = T_c/T_1 = \log p_c/f_1 + 1$. ϕ_1 will therefore be approximately constant unless p_c is abnormal (helium). In the case of fusion, $(v_2 - b_2)/v_2 = 1/14$, where $v_2 - b_2$ is the effective volume for molecular motion. Thence $\phi_2 = T_c/T_2 = 2a_c/\gamma a_2$, where $T_2 = $ m. p., a is the attraction constant, and γ is usually 0·9, but for ideal substances (a and b constant) is 0·5. For ordinary substances, $a_2 = 1·4a_c$; $\phi_2 = 2$. For limiting substances (with T_c from 400 to 500°), $\phi_2 = 1·83$, which agrees with the rule of Timmermans (this vol., ii, 430) that the melting points of different families of substances tend to an upper limit of 117° C.

J. R. P.

A Differential Thermometer. ALAN W. C. MENZIES (*Proc. Nat. Acad. Sci.*, 1921, **7**, 81—83).—A water-filled differential thermometer for use in ebullioscopic measurements is described. The thermometer consists of a length (12 cm.) of stout-walled pyrex glass blown to a bulb at its upper end and bent and enlarged at its lower end. Before sealing, all air is expelled by boiling, so that the pressure generated at either end is due to the vapour of the indicating liquid. Both the stem and the lower bulb are graduated in mm. The various errors associated with the Beckmann thermometer are discussed in connexion with the present instrument.

J. F. S.

Applications of a Differential Thermometer in Ebullioscopy. ALAN W. C. MENZIES and SIDNEY L. WRIGHT (*Proc. Nat. Acad. Sci.*, 1921, **7**, 77—80).—The authors described a modification of the Cotterell ebullioscopic apparatus (A., 1919, ii, 447; 1921, ii, 240) which involves the use of a loose pump which is hung on the lower bulb of a differential thermometer (cf. preceding abstract), a sealed-on condenser attached to the top of the boiling tube, and down the centre of which is a glass rod attached to the thermometer to hold it in position. The bottom of the boiling tube is constricted to form a bulb, which contains the whole of the solvent, and a graduated neck. In this way, the volume of liquid may be read immediately

the ebullition has ceased and before the condensed liquid has had time to drain back into the bulb. The apparatus has no corks in its construction. The authors claim that with this apparatus readings may be obtained as rapidly as fresh portions of the dissolved substance can be weighed, and these have an error not larger than 0·5%. J. F. S.

An Improvement in Barger's Method for the Estimation of Molecular Weight. KARL RAST (*Ber.*, 1921, **54**, [*B*], 1979—1987).—The main innovation consists in the replacement of the individual drops used in the original method (T., 1904, **85**, 286) by a single larger drop which is placed in a capillary tube and is fixed at one end. The variations in the size of the drop are therefore much greater and a single reading only is involved. A further advantage lies in the possibility of using volatile solvents such as ether or pentane, whilst, in addition, less trouble is involved when less volatile solvents are used at increased temperatures.

A capillary tube, 0·5—1·2 mm. in external diameter and 20—30 cm. long, is filled successively to a length of about 5 cm. with the comparison solution, a bubble of air 3—4 mm. long, and then with the solution under investigation to a length of 4—5 cm. The latter is drawn into the tube so as to leave about 3 cm. free. The " comparison " end of the tube is sealed and the other end drawn out to an exceedingly fine capillary, which is broken off so that a length of about 2 cm. remains, and is then sealed. The " comparison " end is broken and the solution allowed to flow down to the fine point, after which it also is drawn out and sealed. The tube is now mounted in a Petri dish, and the observations are made under the microscope as in the original method. It is convenient to have the two solutions of different colours: a suitable standard is provided by azobenzene for all solutions which are not red, and by naphthalene for red solutions. Solvents of low boiling point, for example, ethyl ether, ethyl acetate, acetone, carbon disulphide, alcohol (90%), or a mixture of pyridine and acetone, are particularly serviceable, since the changes then occur with convenient rapidity. If desired, a series of solutions, separated from each other by bubbles of air, may be used in the same capillary. H. W.

A Flame with Very High Temperature. ERNST HAUSER and ERNST RIE (*Sitzungsber. K. Akad. Wiss. Wien*, 1920 [IIA], **129**, 539—547; from *Chem. Zentr.*, 1921, iii, 588).—An inflammable liquid is fed to a specially constructed burner, where it is atomised by means of a chemically indifferent gas (hydrogen) to a horizontal cone. This is invested with a mantle of oxygen blown from the peripheral portion of the burner. A temperature of more than 3000° is thus obtained. Using this flame, carbon was changed into graphite or, under certain conditions, into minute, transparent, highly refracting crystals. G. W. R.

Radiation Theory of Thermal Reactions. W. C. M. LEWIS and A. McKEOWN (*J. Amer. Chem. Soc.*, 1921, **43**, 1288—1306).— A theoretical paper in which an expression is obtained for the

velocity of a unimolecular reaction in a gaseous system, on the basis of the radiation hypothesis of thermal reactions, making use of continuous absorption of radiation by an oscillator. The expression obtained is $k_{uni} = (8\pi^2 e^2 n_m{}^3 \nu^2/3mc^3) \cdot \epsilon^{-h\nu/kT}$, in which k_{uni} is the unimolecular velocity cŏnstant, e and m are the charge and mass of the electron, ν is the frequency of the radiation characteristic of the reaction, k and h are the constants of Boltzmann and Planck, respectively, T is the absolute temperature, and n_m the refractive index of the substance in an ideal state corresponding with the closest possible packing of the molecules. The term n_m is shown to have a value of approximately 200, which is practically independent of the system considered and of the temperature. The expression for the velocity constant agrees with the experimental data of uni-molecular reactions, so far as they are known. By considering reversible reactions of the dissociation type, an expression is obtained for the equilibrium constant which is shown to be in good agreement with the experimental data for iodine given by Bodenstein and Starck (A., 1911, ii, 20). Recent criticisms of the radiation hypo-thesis have been considered and answered. In view of the nature of the criticisms, it is essential to emphasise the distinction rather than the resemblance between thermal and photochemical processes. The resemblance lies in the fact that both processes are attributed to radiation, whilst the distinction enters in the manner and extent to which the transformation of radiant energy occurs. Thus Langmuir attributes the mechanism of a thermal process to rate of emission from a surface, which mechanism, however, characterises photochemical action only. On the other hand, Lindemann considers photochemical action, but regards it from the point of view of radiation density, which is shown to define thermal velocity and not photochemical velocity, when the radiation has the same temperature as the matter.   J. F. S.

Volume of Kations in Permutite. A. GÜNTHER-SCHULZE (*Zeitsch. Physik.*, 1921, **5**, 324—330; cf. this vol., ii, 9).—The molecular volume has been determined at 18° for a number of permutites containing different kations, and from the space taken up by the kation the kation volume has been calculated for lithium, sodium, potassium, ammonium, rubidium, silver, magnesium, calcium, strontium, barium, cadmium, thallium, lead, and uranyl ions. These values are compared with the atom radius and the kation radius. In most cases, the determined kation volume is smaller than the atoɯ̃c volume; only in the case of the four elements with large atomic weights, silver, cadmium, lead, and thallium, is the reverse the case. In the case of lithium, potassium, and rubidium, the atomic radii agree very nearly with those deduced by Lorenz from diffusion experiments in mercury.   J. F. S.

Surface Tensions of Salts of the Fatty Acids and their Mixtures. ERIC EVERARD WALKER (T., 1921, **119**, 1521—1537).

Adsorption of Gas by Charcoal, Silica, and other Substances. HENRY BRIGGS (*Proc. Roy. Soc.*, 1921, [A], **100**, 88—102).—The adsorptive capacities of charcoal and silica at liquid

air temperatures (−150°) were compared, especially as relates to hydrogen and nitrogen. Evaluations were made of the volume of solid matter, the interstitial space between the granules, and the internal gaseous space. The pressure of capillaries is not sufficient to account for adsorption. It is argued that a vitreous solid is a complete atomic linking; activation is considered to be the effect of disrupting the solid polymerides, and the means of accomplishing the partial depolymerisation of charcoal and silica is described.

<div align="right">J. R. P.</div>

Stoicheiometry of Adsorption. II. Adsorption of Potassium and Barium Salts of Various Anions. Sven Odén and E. W. Langelius (*J. Physical Chem.*, 1921, **25**, 385—398; cf. this vol., ii, 438).—The adsorption of the hydroxide, bromide, thiocyanate, nitrate, and chloride of potassium and barium, and the iodide, sulphite, fluoride, ferrocyanide, citrate, chromate, sulphate, and chlorate of potassium by charcoal has been determined by the interferometric method previously described (*loc. cit.*). In the case of the potassium salts, the concentration–adsorption curves cross one another, that is, the order of adsorption varies with concentration. With a concentration $0.010M$, the order is : fluoride < chloride < sulphate < nitrate < chloride < bromide < ferrocyanide < citrate < chlorate < chromate < iodide, whilst at $0.2M$ the order is : sulphate < fluoride < ferrocyanide < chloride < bromide < chromate < citrate < nitrate < chlorate < iodide < cyanide. In the case of the barium salts, the order of adsorption does not change with change in concentration, except perhaps in the case of the acetate, and the order is the same as that for the potassium salts at the concentration $0.05M$; the order is : chloride < bromide < acetate < nitrate < thiocyanate < hydroxide.

<div align="right">J. F. S.</div>

Adsorption by Precipitates. IV. Harry B. Weiser (*J. Physical Chem.*, 1921, **25**, 399—414; cf. A., 1920, ii, 228; 1919, ii, 269).—A number of experiments on the adsorption of oxalate, chromate, and dichromate ions by hydrated ferric oxide are described, and experiments are also described on the quantities of electrolytes required to coagulate a colloid. It is shown that the amount of electrolyte required to coagulate a colloid is influenced by the rate of addition. Since a quantity of electrolyte that will cause complete coagulation when the addition is rapid will not cause complete coagulation when the addition is slow, the colloid is said to have become acclimatised, and the phenomenon is termed acclimatisation. This term is a misnomer, since the colloid does not become acclimatised to the presence of the electrolyte in the ordinary sense of the word. The amount of precipitating ion carried down by a colloid is determined by the adsorption of the electrically charged particles during neutralisation and the adsorption of the electrically neutral particles during agglomeration. The adsorption of oxalate, chromate, and dichromate by hydrated colloidal ferric oxide emphasises the importance of adsorption by neutralised particles in

determining the amount of electrolyte carried down by a precipi-
tated colloid. The drop-by-drop addition of an electrolyte to a
colloid over a long period is accompanied by fractional precipitation
of the colloid and the precipitating ion. The precipitation value
is such a concentration of precipitating ion added all at once that
sufficient adsorption to cause neutralisation of the colloidal particles
can take place promptly. The necessity for using more electrolyte
to effect complete precipitation on slow addition arises, not from
the adaptability of the colloid to the presence of the electrolyte,
but from the fact that the fractional precipitation during slow
addition continually removes ions owing to adsorption by the
neutralised particles during agglomeration; and this loss must be
compensated. The excess of electrolyte required for a given slow
rate of addition is determined by (a) the extent to which the colloid
undergoes fractional precipitation, (b) the adsorbing power of the
precipitated colloid, and (c) the adsorbability of the precipitating
ion. The amounts adsorbed at the precipitating concentration of
the various ions are not equivalent, as Freundlich assumes.
Adsorption of equivalent amounts effects neutralisation of the
charged particles, but adsorption during agglomeration varies with
the concentration and adsorbability of the ion. Comparable
adsorption values cannot be obtained at the precipitation concen-
tration on account of the variability of the latter.   J. F. S.

Method of Photographing Transparent Crystals. M.
FRANÇOIS and CH. LORMAND (*Bull. Soc. chim.*, 1921, [iv], **29**, 792–
807).—Full details are given for the photomicrography of transparent
crystals. A simple apparatus is described and illustrated, including
a method of illuminating the crystals. Instructions are given as
to choice of plates, method of development, and a method for
calculating the time of exposure.   W. G.

Determination of Crystal Structures by Means of X-Rays.
M. VON LAUE (*Naturwiss.*, 1920, **8**, 968—971; from *Chem. Zentr.*,
1921, iii, 505—506).—A theoretical discussion showing the limita-
tions of the X-ray method for the determination of crystal structures.
It is pointed out that the lattice image is not a refraction, but an
interference, image. Information as to crystal structure is actually
obtained by considering the results obtained with rays falling at
different angles and of different wave-lengths. Additional informa-
tion is given by chemical constitution, the dispersive power of the
atoms present for the rays used, crystal form, and the mathematical
theory of simple and compound space lattices.   G. W. R.

**The Chemical Reactions of Crystals and their Relation
to the Molecular Structure.** F. RINNE (*Z. Metallk.*, 1921, **13**,
401—406).—A theoretical paper dealing with the arrangement
of the atoms and molecules in crystals and their relation to the
symmetry of the crystal. It is shown that the action of reagents
on crystals takes place in a symmetrical manner and if carried out
slowly results in the development of symmetrical figures on the
surface of the crystals which vary according to the relation of the

face attacked to the axes of the crystal.   An explanation of this and of the change of crystal form that some minerals undergo on heating is given, based on the space-lattice theory of crystal structure.

<div align="right">A. R. P.</div>

Methods for [Effecting] the Orientation of Crystal Elements. R. BECKER, R. O. HERZOG, W. JANCKE, and M. POLÁNYI (*Zeitsch. Physik*, 1921, **1**, 61—62).—Several methods are described whereby an axial orientation of crystal elements in various types of substances may be produced. 1. A crystalline powder placed in a magnetic field so arranges itself that individual crystalline particles take up positions corresponding with the inductive action. 2. Subjecting crystalline powders and substances like wax and paraffin to high pressures (4000—5000 atms.) brings about a marked regular arrangement of the particles.   This is observed in the case of the substances succinic acid, indigotin, and stearic acid. 3. The cold drawing of metals produces an axial symmetry of the elementary crystals of the metals.

<div align="right">J. F. S.</div>

Constitution of Mixed Crystals and the Space Filling of the Atoms. L. VEGARD (*Zeitsch. Physik*, 1921, **5**, 17—26).— A continuation of previous work (A., 1917, ii, 243).   In the present paper the structure of mixed crystals of potassium bromide and chloride, potassium and ammonium chloride, and potassium and ammonium sulphate has been examined by means of X-ray spectra, using the Debye-Scherrer powder method.   The reflection maxima have been photographed for the mixed crystals named above and their components.   The results indicate the replacement of one atom by another in mixed crystals is irregular and unordered, so that mixed crystals are to be defined as those substances which are characterised by an unordered atomic substitution.   The change of the position of the reflection maxima denotes a change in the molecular volume.   The replacement of bromine by chlorine effects a contraction, whilst the replacement of potassium by ammonium effects an expansion of the crystal lattice.   The length of the side of the elementary lattice of the mixed crystals of potassium bromide and chloride is given with great accuracy by the formula $a_m = (p-100)/100 \cdot a_{KBr} + p/100 \cdot a_{KCl}$, in which p is the molecular per cent. of the potassium chloride in the mixed crystal and a_m, a_{KCl}, a_{KBr} are respectively the lengths of the sides of the lattices of the mixed crystal, potassium chloride, and potassium bromide. The crystal lattice of ammonium chloride is shown to be a cubic chlorine lattice centred round a similar nitrogen lattice.   It is shown that the ammonium radicle takes up more space in the ammonium chloride lattice than in that of the face-centred type. The diameter of the hydrogen atom is calculated from the data obtained for ammonium chloride and bromide and values between 1·58 Å.U. and 1·68 Å.U. obtained.

<div align="right">J. F. S.</div>

The Colloid Mill and its Applications. HERMANN PLAUSON (*Zeitsch. angew. Chem.*, 1921, **34**, 469—472; 473—474).—Two types of machine are described, designed for the preparation of

colloidal solutions by mechanical means. The first type, suitable for dispersing typical colloids in a suitable dispersion medium, depends on the hammer-and-anvil principle, whilst the second, which depends on friction, is suitable for the preparation of colloidal solutions of such substances as minerals, dyes, or carbon. It is shown that definite saturated colloidal solutions can be prepared by means of such machines, but that the saturation limit can be raised by the addition of dispersion accelerators or " dispersators," which may be compared in their action with chemical catalysts. Numerous technical applications of the colloid mill are discussed, especially a new application in the viscose artificial silk process. With a suitable dispersion medium, cellulose can be reduced in the colloid mill to the colloidal form, and in this state it reacts with the theoretical quantity of alkali to form alkali cellulose which in turn reacts smoothly with carbon disulphide to give xanthogenate without the formation of any thio-salts as by-products. [Cf. *J. Soc. Chem. Ind.*, 1921, Nov.]   E. H. R.

The Hydration of the Fibres of Soap Curd. III. Sorption of Sodium Palmitate. MARY EVELYN LAING (T., 1921, 119, 1669—1676).

Statistical Mechanics and Chemistry. E. P. ADAMS (*J. Amer. Chem. Soc.*, 1921, 43, 1251—1254).—A theoretical paper in which the view is advanced that if the laws of chemical dynamics are found to be consistent with the principles of statistical mechanics it is not only unnecessary, but even unjustifiable, to introduce the quantum hypothesis to derive these laws. The author shows that Tolman's criticism (this vol., ii, 99) of Marcelin's attempt (A., 1915, ii, 328) to base a theory of chemical dynamics on the principles of statistical mechanics, is unfounded. The main point of Tolman's criticism is that Marcelin has confused Gibbs's canonical distribution of an ensemble of systems with the Maxwell-Boltzmann distribution. The author shows that the form of the Maxwell-Boltzmann law used by Marcelin may be derived without making any use of the canonical distribution of Gibbs.   J. F. S.

A Piezoelectric Method of Measuring Explosion Pressures. DAVID A. KEYS (*Phil. Mag.*, 1921, [vi], 42, 473—488).—The piezoelectric properties of tourmaline crystals were used in conjunction with a special form of cathode ray oscillograph to record the pressures developed in explosions and the velocity of explosion waves in water. [See *J. Soc. Chem. Ind.*, 1921, 760A.]   J. R. P.

Gaseous Combustion at High Pressures. II. The Explosion of Hydrogen–Air and Carbon Monoxide–Air Mixtures. WILLIAM ARTHUR BONE and WILLIAM ARTHUR HAWARD (*Proc. Roy. Soc.*, 1921, [A], 100, 67—84; cf. A., 1915, ii, 684).—The rise of pressure in the explosion of mixtures of hydrogen and air occurs very rapidly, but there is evidence of development of heat for a short period after the attainment of the maximum pressure. The rise of pressure in the explosion of carbon monoxide and air occurs

much more slowly, and cooling is delayed for a long period after the maximum pressure has been reached. The presence of even 1% of hydrogen in the carbon monoxide–air mixture, at the high initial pressures employed, accelerates the rise of pressure on explosion to a high degree. A theory is proposed to account for the different modes of explosion of hydrogen and carbon monoxide.

J. R. P.

The Propagation of Flame in Mixtures of Ethylene and Air. WILLIAM RONALD CHAPMAN (T., 1921, **119**, 1677—1683).

A Periodic Reaction in Homogeneous Solution and its Relation to Catalysis. WILLIAM C. BRAY (*J. Amer. Chem. Soc.*, 1921, **43**, 1262—1267).—The action of hydrogen peroxide both as an oxidising agent and as a reducing agent has been studied in the case of its reaction with iodine. The reactions which occur are (1) $5H_2O_2+I_2=2HIO_3+4H_2O$ and (2) $5H_2O_2+2HIO_3=5O_2+I_2+6H_2O$. It is shown that far more peroxide disappears from the reacting system than can be accounted for by the above equations, consequently the reaction (3) $H_2O_2 \longrightarrow H_2O+\frac{1}{2}O_2$ must also take place and this is catalysed by the iodic acid–iodine couple. Using a mixture containing $0.190M$ hydrogen peroxide and $0.094M$ potassium iodate, the reaction was carried out at $60°$ in the presence of varying concentrations of sulphuric acid by measuring the rate of evolution of oxygen. In the case of $0.055N$-sulphuric acid, it is found that after an induction period lasting a very short time the reaction takes place rapidly and smoothly; its rate is proportional to the concentration of both hydrogen peroxide and iodate, and is but little affected by the concentration of hydrogen ion above $0.2N$. With a concentration of $0.110N$-sulphuric acid, after the induction period (seven minutes) the reaction proceeds smoothly, and a faint permanent iodine coloration is observed, but the velocity of evolution of oxygen is much greater than in the case of an acid concentration $0.055N$. With acid concentrations intermediate to the foregoing, the velocity of evolution of oxygen is not uniform, but periodic in nature. Taking acid concentrations $0.073N$ and $0.0916N$ respectively, it is found that the induction period is eighteen and twelve minutes respectively, and then the evolution of oxygen is periodic. The curves representing this show a series of relatively flat portions followed respectively by very steep portions. In the flat regions the colour due to iodine slowly deepens and in the steep regions slowly fades away. With the more dilute acid, the period is between three and three and a half minutes, but with the more concentrated acid the period slowly increases from ten to thirteen minutes. Thus with $0.055N$-acid there is no periodicity, with $0.070N$-acid there are periods of ten to thirteen minutes, with $0.0916N$-acid periods of three to three and a half minutes, and with $0.110N$-acid there is pure catalysis and no detectable periodicity. In the last case, however, it is likely that after a very short induction period the reaction consists of a large number of very short periods. This periodicity is taken

as furnishing direct evidence in favour of the intermediate compound hypothesis of catalysis. An experiment carried out at 25° shows that the periods may be made to extend over several days, and when no shaking takes place the oxygen does not leave the solution in bubbles, thus making the reaction strictly homogeneous.

J. F. S.

The Effect of Temperature on Platinum Black and other Finely-divided Metals. ROBERT WRIGHT and ROBERT CHRISTIE SMITH (T., 1921, **119**, 1683—1688).

Adsorption of Gases by Metallic Catalysts. HUGH STOTT TAYLOR and ROBERT MARTIN BURNS (*J. Amer. Chem. Soc.*, 1921, **43**, 1273—1287).—Measurements of the adsorption of hydrogen, carbon monoxide, carbon dioxide, and ethylene by finely-divided nickel, cobalt, iron, copper, palladium, and platinum have been made at various temperatures with the object of finding the relationship this phenomenon bears to catalytic activity, and particularly to the mechanism involved in hydrogenation reactions. It is shown that adsorption by these metals is a specific property quite different in nature from adsorption by inert adsorbents such as charcoal. The extent of the adsorption is shown to be a function of the mode of preparation, and is especially less pronounced the higher the temperature of preparation of the finely-divided metal. The relationship between this fact and the corresponding facts of catalytic behaviour has been pointed out. The adsorption isotherms have been studied in the cases, nickel and hydrogen and copper and carbon monoxide. In both cases, adsorption increases rapidly with increasing partial pressure below 300 mm., and becomes practically independent of pressure above this point. The significance of irreversible adsorptions of gases has been studied, and reasons are suggested for divergences between different catalysts. It is indicated that, in addition to the adsorption factor, it is necessary to consider some other factor in explaining catalytic activity, and it is shown that a combination of the temperature factor with the adsorption factor in catalytic action suggests a possibility of explaining the divergence between the catalytic activities of various metals. J. F. S.

Catalytic Hydrogenation of Organic Compounds with Common Metals at the Temperature of the Laboratory. The Activity of Nickel Catalysts prepared at Different Temperatures. Influence of Oxygen on the Nickel Catalyst. IV. C. KELBER (*Ber.*, 1921, **54**, [*B*], 1701—1705; cf. A., 1917, ii, 215).—Willstätter and Waldschmidt-Leitz (this vol., ii, 187) have reduced nickel oxide, prepared by ignition of nickel oxalate, to metallic nickel at 350—360°, and describe the product as incapable of accelerating hydrogenation catalytically unless previously primed with air. The author has been unable to confirm their observations. He has further examined the behaviour of metallic nickel obtained by the reduction of basic nickel carbonate at different temperatures, the operation being effected in

the same vessel as is used for the subsequent hydrogenation experiments, thus avoiding any possible complication caused by exposing the product to air. The activity of the catalyst is examined in the case of aqueous solutions of sodium cinnamate. It is found that metallic nickel prepared at 350—360° is but little inferior in activity to that obtained at 300°, and notably superior to that produced at 210°. The material first described becomes completely inactive when shaken with oxygen at 18—20°, but, if treated with hydrogen at 70—80°, it becomes again active at the temperature of the laboratory. The latter phenomenon was not observed by Willstätter and Waldschmidt-Leitz, since they worked at 60°, a temperature at which the catalyst commences to regain activity.

H. W.

The Influencing of the Activity of Catalysts. IV. Oxidative Catalytic Dehydrogenation of Alcohols. II. KARL W. ROSENMUND and FRITZ ZETZSCHE (*Ber.*, 1921, **54**, [*B*], 2033—2037; cf. this vol., ii, 393).—Catalytic dehydrogenation by means of copper, quinoline, and nitro-compounds and oxygen leads to the production of aldehydes from primary aliphatic, aromatic, and heterocyclic alcohols and of ketones from secondary alcohols whereas tertiary alcohols remain unchanged. The method is useful in the cases of difficultly volatile or non-volatile alcohols, but has no advantage over the older processes when the more volatile alcohols are used.

Benzhydrol is almost quantitatively transformed into benzophenone when heated with quinoline and nitrobenzene in a current of oxygen; under similar conditions, triphenylcarbinol is unaffected. The yields of acetaldehyde, propaldehyde, and *iso*butaldehyde are 52%, 57%, and 75% respectively, but the volatility of the corresponding alcohol at the temperature necessary for the reaction renders the completion of the change difficult to secure. Fermentation amyl alcohol gives an 80% yield of the corresponding aldehyde. *o*-Chlorobenzyl alcohol (p-*nitrobenzoate*, yellow, monoclinic prisms, m. p. 93—94°), is converted into *o*-chlorobenzaldehyde (yield 86·2%), whereas furfuryl alcohol gives a 74% yield of furaldehyde.

Considering the number of factors involved in the reactions, it is not surprising to find considerable fluctuations in the optimal temperature for each change. The lower limit may be considered to lie at 125—130°, at which amyl alcohol is dehydrogenated; benzylhydrol and furfuryl alcohol give satisfactory results at 145°, benzyl alcohol at 165°, and *o*-chlorobenzyl alcohol at 195°; the upper limit of temperature is 180° and 165° in the cases of benzyl alcohol and furfuryl alcohol respectively. H. W.

The Influencing of the Activity of Catalysts. V. Catalytic Reduction of Esters and Aldehydes. KARL W. ROSENMUND, FRITZ ZETZSCHE, and F. HEISE (*Ber.*, 1921, **54**, [*B*], 2038—2042).—It has been shown previously (this vol., ii, 362) that the reduction of benzoyl chloride to benzyl alcohol is complicated by the reductive fission of benzyl benzoate (formed from unchanged benzoyl chloride

and benzyl alcohol) to benzoic acid and toluene, and by the formation of dibenzyl ether. The first-named reaction is shown in the cases of benzyl benzoate and benzhydryl benzoate to take place readily in the presence of xylene and more slowly in the presence of toluene; it is almost completely inhibited by the addition of quinoline. Benzaldehyde is converted by hydrogen in the presence of palladium and xylene mainly into dibenzyl ether, the production of which is hampered whilst that of benzyl alcohol is facilitated by increasing addenda of quinoline; more powerful regulators, such as " sulphured " quinoline, inhibit the formation of dibenzyl ether. Benzyl alcohol is converted into dibenzyl ether by palladium. The reduction of benzoyl chloride may be represented by the scheme: hydrocarbon $\longleftarrow$ ester $\longleftarrow$ benzoyl chloride $\longrightarrow$ aldehyde $\longrightarrow$ alcohol $\longrightarrow$ ether; any particular member of the series may be made the main product of the change by suitably influencing the catalyst.

H. W.

Non-radiating Atoms. (SIR) JOSEPH LARMOR (*Phil. Mag.,* 1921, [vi], **42**, 595).—The conditions under which an orbital system of electrons does not radiate energy unless disturbed are discussed.

J. R. P.

Escapements and Quanta. (SIR) JOSEPH LARMOR (*Phil. Mag.,* 1921, [vi], **42**, 592—594).—An atom is compared with a clock, the outer electron shell being the pendulum, maintained in continuous vibration by the energy of the core imparted through an unknown escapement mechanism, which parcels out quanta.

J. R. P.

An Atomic Model based on Electromagnetic Theory. I. ALBERT C. CREHORE (*Phil. Mag.,* 1921, [vi], **42**, 569—592).—A mathematical paper. It is shown that the force between two neutral atoms each composed of revolving rings of electrons and stationary charges is not zero on the basis of Saha's theory of the forces (*Physical Rev.,* 1919, **13**, 41). There cannot then be an equilibrium velocity for a ring of electrons, and an atom with stationary electrons is indicated. A model of the hydrogen atom consistent with electromagnetic theory consists of two electrons ($-e$) of the shape of oblate spheroids, one on each side of a smaller positive nucleus ($+2e$) of similar shape, the whole rotating about a common axis. The attractions between such atoms would obey the inverse square law.

J. R. P.

Helium and Hydrogen Models. EDWIN C. KEMBLE (*Science,* 1920, **52**, 581—583).—Closely approximating expressions for the energy of the electrons in Langmuir's model of the helium atom (A., 1920, ii, 656; *Science,* 1920, **52**, 433) are derived from the Wilson-Sommerfeld quantum conditions. Numerical evaluations using Langmuir's data do not give the observed ionisation potential of helium.

CHEMICAL ABSTRACTS.

Scattering of Light in Gases. M. BORN and W. GERLACH (*Zeitsch. Physik,* 1921, **5**, 374—375).—A theoretical paper in which

the scattering of light has been calculated on the basis of the hydrogen, oxygen, and nitrogen models of Bohr and Debye. The depolarisation factor deduced from the figures obtained has been compared with the experimental figures found for this factor by Strutt and Gans. The comparison shows that the order of magnitude is the same in both cases, but neither is there a quantitative agreement nor is the sequence the same for the three models. It is therefore shown that the molecule models do not represent the reality.   J. F. S.

The **Determination of the Valency Scale of Iron, Cobalt, Nickel, Copper, Manganese, Tin, and Tungsten by means of their Water Vapour Equilibria, and of the Dissociation Pressure of the Oxides of these Metals.** LOTHAR WÖHLER and O. BALZ (*Zeitsch. Elektrochem.*, 1921, 27, 406—419).—Experiments were made to determine the true number of oxides of iron by measuring the equilibrium constants when ferric oxide is reduced by a gradually increasing amount of hydrogen, or, conversely, when iron is oxidised by an increasing amount of water vapour. The equilibrium constant was determined by measuring the concentrations C_{H_2O} and C_{H_2} of water vapour and hydrogen respectively in equilibrium with the solid phase. The apparatus used was similar to that previously described by Wöhler and Prager (A., 1917, ii, 455). Only three equilibrium constants were found, corresponding with equilibria Fe_2O_3/Fe_3O_4, Fe_3O_4/FeO, and FeO/Fe, the first being the highest, numerically, and the second the lowest. Since, in the experiments, a known weight of ferric oxide was taken, and known volumes of hydrogen for the reduction, the exact composition of the solid phase could be determined when the value of the equilibrium constant changed. In this way it was shown that the only oxides of iron formed, either by reduction or oxidation, were FeO, Fe_3O_4, and Fe_2O_3. The primary product of oxidation of iron with water vapour at a red heat is FeO, not Fe_3O_4 as has been stated. The values of the equilibrium constants C_{H_2O}/C_{H_2} found were, for Fe_2O_3/Fe_3O_4, 7·5 at 350° to 17·9 at 950°; for Fe_3O_4/FeO, 1·03 at 640° to 5·07 at 950°; for FeO/Fe, 0·62 at 750° to 0·92 at 990°.

The same method was also applied to determining the valency scales of other metals. The highest oxide of cobalt, Co_2O_3 was too unstable for equilibrium determinations. The constants for Co_3O_4/CoO and CoO/Co were determined at 450°, the values being respectively 34·4 and 13·5. No other oxide of cobalt was found. In the case of nickel, the oxide Ni_3O_4 was too unstable for determinations to be made, since it begins to decompose below 450°. The value of the constant for NiO/Ni is about 14·8 at 450°. The so-called nickel sub-oxide is a mixture of NiO and metal. From the fact that Ni_3O_4 is less stable than Co_3O_4 it may be concluded that nickel is nobler than cobalt.

In the case of copper oxides, the following constants were found at 450°: CuO/Cu_2O, 26·3; Cu_2O/Cu, 16·7. In the manganese series the only constant determined was Mn_3O_4/MnO at 450°, 34·6.

Stannous oxide was found to be a stable intermediate stage between tin and stannic oxide, both in oxidation and reduction, the values found being, for SnO_2/SnO, 13·6, and SnO/Sn, 7·9, both at 700°. In the case of tungsten, between tungsten trioxide and the metal, only the bluish-violet W_2O_5 and the brown WO_2 were found as stable phases. The blue oxide with an oxygen value between WO_3 and W_2O_5 is a mixture. The values found were, WO_3/W_2O_5, about 16·0 at 800°; W_2O_5/WO_2, about 5·0 at 800°; WO_2/W, about 1·0 at 950°.

Applying van't Hoff's equation, the heat of reaction for the equation $Fe + H_2O = FeO + H_2$ was calculated from the temperature coefficient of the equilibrium constant, and agreed well with values calculated from other data. In the case of the reaction $3FeO + H_2O = Fe_3O_4 + H_2$, the values calculated for the heat of reaction agreed less well, probably because the temperature coefficient of the specific heat of the solid phase introduced an unknown error. The dissociation pressures of the different oxides were also calculated. For the oxides of tin, iron, and tungsten at 1000° these are of the order of 10^{-11} to 10^{-12} mm. of mercury.   E. H. R.

New Apparatus for the Generation of Gas. F. HAHN (*Chem. Zeit.*, 1921, **45**, 992).—The numerous forms of apparatus proposed for the generation of gases by the action of liquids on solids are essentially modifications of either Kipp's or Küster's apparatus. Kipp's apparatus has the disadvantage that the acid cannot be completely exhausted, as it is in Küster's apparatus, owing to the mixing of used and fresh acid, whilst Küster's apparatus has the serious disadvantage that, after the gas generated while the apparatus is at rest has been delivered, for some time as much acid must be run in as the volume of the gas delivered, and consequently, when the gas is shut off, the apparatus cannot contain the gas which continues to be generated. These disadvantages are avoided in the new apparatus, which may be of either the Kipp or Küster type. In the former case, the connecting tube from the upper globe is bent slightly to one side and reaches to the bottom of the middle compartment. The middle compartment is connected to the bottom compartment by a tube, the top of which is above the level of the liquid when the apparatus is not in use, and there is a fine orifice somewhat below the upper end of the tube.   F. M. R.

Improvements in the Soxhlet Extraction Apparatus. OSKAR HAGEN (*Zeitsc.*. *angew. Chem.*, 1921, **34**, 499—500).—An improved form of the extraction apparatus described previously (this vol., ii, 104). The syphon is done away with, and the condensed solvent dropping from the condenser is not allowed to accumulate in the extraction cylinder, but flows down immediately into the flask after percolating through the material. By this means extraction can be completed in from one-quarter to two-thirds of the time required by the old apparatus. The outlet from the extraction chamber to the flask is bent into a convolution to serve the double purpose of forming a trap to prevent the vapour from the flask rising through the extraction chamber, and, by means of a two-way

tap situated at the top of the loop, to provide a means of with-drawing for testing purposes a sample of the liquid leaving the extraction cylinder.   All joints in the apparatus are ground in, as even the best quality corks yield about 10% of their weight in extractive matter to ether.   G. F. M.

Inorganic Chemistry.

Some Negative Attempts to Transmute Elements in accordance with Marignac's views on the Unity of Matter. E. BRINER (*J. Chim. physique*, 1921, **19**, 9—10).—The action of an electric arc on iodine vapour and a mixture of helium and hydrogen produced no transmutation, although the temperatures of isolated molecules must have been very high.   J. R. P.

Rapid Method for Determining the Density of Air. GREGORY P. BAXTER (*J. Amer. Chem. Soc.*, 1921, **43**, 1317—1318).—A rapid method for determining the density of the air is described.   A sealed globe of known exterior volume is weighed under accurately known conditions of temperature, pressure, and humidity.   From the conditions, the density of the atmosphere at the time of weighing and the buoyancy effect of the air on the globe and weights may be calculated.   By adding the difference between the buoyancy effect on the globe and on the weights to the weight of the globe in air, the weight of the globe in a vacuum is found.   If the globe is weighed in the air under any conditions, the weight of air displaced by the globe in excess of that displaced by the weights is readily found by subtraction from the weight in vacuum.   This difference divided by the volume of the globe less the volume of the weights yields the atmospheric density.   Numerical examples illustrating the method are given in the paper.   J. F. S.

Variations of Density of Atmospheric Air. A. JAQUEROD and CH. BOREL (*J. Chim. physique*, 1921, **19**, 11—28).—The variations of density of the air in the region of Neuchâtel follow the Loomis-Morley law.   The amplitude of the variations does not usually exceed 0·5—0·6 mg.   The same result was found with air taken at 2000—5000 m., but the amplitude is smaller.   The explanation which assumes the presence of a heavy gas must be rejected and the presence of ultramicroscopic dust is suggested.   J. R. P.

Oxidation of Sulphites in Concentrated Solutions. J. MILBAUER and J. PAZOUREK (*Chem. Listy*, 1921, **15**, 34—38).—Concentrated solutions of sulphites are oxidised slowly but quite constantly at ordinary temperatures by air. (Cf. Lumière and Seywetz, *Rev. gen. chim.*, **7**, 15.) Cobalt sulphate, used in concentrations of 0·01 and 0·001 molar, acts as a positive catalyst for

this reaction. Manganese and copper salts, contrary to results obtained with dilute solutions by Bigelow (A., 1898, ii, 506) and Schilow (A., 1903, ii, 276), are not very active catalysts in concentrated solutions of sulphites. In concentrated solutions 0·5 molar, weak alkalinity of the medium intensifies the oxidation, if no precipitation of the catalysing agent is caused. Strong alkalinity retards the reaction. An acid medium has a similar influence. The rapidity of the reaction increases with rising temperatures.

CHEMICAL ABSTRACTS.

Colloidal Selenium. A. GUTBIER and R. EMSLANDER (*Ber.*, 1921, **54**, [*B*], 1974—1978; cf. Meyer, A., 1913, ii, 1048; Gutbier and Emslander, A., 1914, ii, 264).—Very stable colloidal solutions of selenium may be prepared by the regulated action of concentrated hydrazine hydrate solution on selenium dioxide or gray, crystalline selenium and subsequent dilution of the solutions with water and purification by dialysis. According to the degree of dispersivity, the colour of the solutions varies from intense yellow to blood-red. The dilute solutions are stable at the boiling point, but are readily coagulated by barium sulphate. The action of electrolytes at the atmospheric temperature has been investigated by mixing 2N-solutions of them with an equal volume of the dialysed system. Hydrochloric, nitric, sulphuric, selenious, and acetic acids immediately change the yellow colour to pink which becomes violet and then blue when the mixtures are gently warmed, thus indicating the formation of coarser aggregates; ammonia has no effect, sodium hydroxide lightens the colour slightly, whereas barium hydroxide causes immediate separation. The coagulating effect of calcium chloride, barium chloride, and alum is particularly marked, whereas that of sodium and potassium chlorides is weaker. Sodium and potassium carbonates appear to increase the stability of the system. The preparations can be frozen to a blue ice, which melts with complete coagulation. With dilute solutions of selenium, on the other hand, the presence of hydrochloric acid, sodium carbonate, or potassium chloride exerts a protective effect in this connexion which is at a maximum at certain definite concentrations; with more concentrated solutions, however, the optimum effect is less definite.   H. W.

Tellurium Sub-bromide. A. DAMIENS (*Compt. rend.*, 1921, **173**, 583—586).—Tellurium sub-bromide, TeBr$_2$, has now been isolated in the solid state, either by rapidly cooling its vapour in a dry vacuum to —80° or by reduction of the tetrabromide in dry ethereal solution in the dark with finely-divided tellurium. The sub-bromide so obtained is chocolate-brown in colour and is decomposed by water. It is completely soluble in dry ether, but it is unstable in this solution, readily decomposing to give tellurium and tellurium tetrabromide. In ethereal solution it combines with iodine to give *tellurium iodobromide*, which is completely soluble in ether and crystallises from it in red crystals.   W. G.

Oxidation and Luminescence of Phosphorus. II. HARRY B. WEISER and ALLEN GARRISON (*J. Physical Chem.*, 1921, **25**, 349—384; cf. this vol., ii, 248).—The various types of emission of phosphorus during oxidation have been considered historically and experimentally from four points of view, (i) emission of gaseous ions, (ii) emission of penetrating radiations, (iii) emission of phosphorus emanation, and (iv) emission of light. It is shown that gaseous ions are formed during the oxidation of phosphorus, and these account for the conductivity of "phosphorised air." These ions furnish nuclei about which oxides and water vapour condense, forming clouds. The cloud arising from glowing phosphorus contains equal numbers of positive and negative particles if the phosphorus is not charged. Ions are formed in the reaction zone and may be withdrawn by an electric field against a current of air sufficiently rapid to remove oxide particles and ozone. The decomposition of ozone and the action of ultra-violet light are unimportant as sources of ions in "phosphorised air." The luminescence of phosphorus is not changed appreciably by charging the element. Radiations of the nature of radium rays, which penetrate black paper and thin metal plates, are not formed during the oxidation of phosphorus. The darkening of a photographic plate protected from light in the region of glowing phosphorus is due to the action of the vapours of hydrogen peroxide and phosphorous oxide. Ions are formed during the oxidation of phosphorous oxide, and render the surrounding atmosphere a conductor. No evidence was obtained of the formation of phosphorus emanation by the action of moisture on phosphorous oxide. The vapours of phosphorous oxide diffuse readily and when admitted to an electrometer they diffuse throughout the instrument and condense on the insulation. On the addition of moisture, the condensed vapours are converted into acid, which causes a leak across the insulation that is easily mistaken for a gaseous leak due to ionisation. The complete oxidation of phosphorus takes place in two stages, phosphorous oxide being the intermediate product. The first step in the oxidation takes place without the emission of light; the luminescence of oxidising phosphorus is due to the oxidation of phosphorous oxide. Ozone is formed during the oxidation of phosphorous oxide. The failure of certain investigators to detect the formation of ozone in this reaction is due, probably, to the action of phosphorous oxide vapours with the iodine liberated in the usual starch–iodide test. Ozone is formed by the ultra-violet light emitted by glowing phosphorus.   J. F. S.

Coagulation of Arsenious Sulphide Sols by Cobaltic Complexes. KICHIMATSU MATSUNO (*J. Coll. Sci. Tokyo*, 1921, **41**, 11, 1—15).—The relationship between the valency of a large number of cobaltammines and their power of coagulating arsenic sulphide sols has been investigated. The effect of ageing of the sol was eliminated by using only such sols as had been kept for a year. The results show that the limiting concentration of the precipitating solution can be expressed by the formula $S_N = S/N^4$, where S_N is

the equivalent concentration of an N valent ion, N the valency of the complex ion, and S the limiting concentration for a univalent ion. This equation may be theoretically deduced from Freundlich's adsorption hypothesis. Using the coagulation method, the author has determined the valency of a number of simple and complex cobaltammine radicles. The chemical changes occurring in aqueous solutions of some of the cobaltammines has been followed by the coagulation method, and the results confirm those obtained in the spectroscopic and conductivity experiments (cf. this vol., ii, 644).

J. F. S.

Metallic Hydrides. I. Alkali Hydrides. FRITZ EPHRAIM and EDUARD MICHEL (*Helv. Chim. Acta*, 1921, **4**, 762—781).—The pure hydrides of sodium and potassium have been previously prepared in very small quantities only (Moissan, A., 1902, ii, 136; Elster and Geitel, A., 1910, ii, 379; Keyes, A., 1912, ii, 627). The former is best obtained by leading a rapid stream of hydrogen directly on to the surface of, not into, the metal at such a temperature, above 350°, that a yellow glow is produced, and the hydride is carried away as a white smoke, which is precipitated electrically and filtered through glass wool. At higher temperatures, the vapour is darker owing to volatilisation of metal. Sodium prepared from its azide had no special advantage for this purpose, and negative results were obtained by the use of sodium amalgam or solutions of the metal in liquid ammonia. Potassium hydride was prepared by leading the gas into the metal at 350°. In each case, reaction was facilitated by the presence of metallic calcium. The hydrides of rubidium and cæsium were prepared by heating a mixture of their carbonates with metallic magnesium in hydrogen at 650° for five days and at 580—620° for three days, respectively (cf. Moissan, A., 1903, ii, 367), when 90% and 48% of gas were respectively absorbed. The following are given as the most trustworthy of the results (in mm.) obtained from vapour tension, measurements at intervals of 10° over the ranges of temperatures indicated: Sodium hydride, 300—410°, 15, 17, 21, 27, 38, 55, 87, 136, 201, 285, 396, 540. Potassium hydride, 350—410°, 56, 83, 120, 168, 228, 308, 430; 415°, 509. Rubidium hydride, 370—450°, 100, 114, 130, 160, 200, 253, 322, 424, 567. Cæsium hydride, 340—440°, 78, 100, 126, 160, 202, 256, 317, 402, 503, 630, 787. The results show that there is little or no difference between the values for the different hydrides, and that removal of hydrogen causes some, but no extensive, diminution of the vapour tension, this being less the smaller the atomic weight of the metal, and according with the view that the metal is soluble in the hydride. Previous measurements (Keyes, *loc. cit.*; Troost and Hautefeuille, A., 1874, 767) have really been carried out with such solutions. The results with rubidium and cæsium are quoted with reserve owing to the possibility of the presence of carbon dioxide from the magnesium carbonate formed, although this dissociates very slowly (Marc and Simec, A., 1913, ii, 708); soda-lime was employed to diminish its effect, and the recorded values were quickly attained.

In the case of rubidium, a noteworthy peculiarity, confirmed by repeated observation, consisted in a rapid increase of pressure up to 85 mm. at 230°, followed by a very gradual increase to 100 mm. at 370°, succeeded by rapid increases as above quoted. The reason for this is left indefinite. The results obtained with cæsium hydride are further affected by the considerable sublimation of the metal itself, and also by its solution in the hydride. The latter effect is much more marked in the cases of rubidium and cæsium than in the others. The stability of the pure hydrides increases from cæsium to sodium. J. K.

Alteration of Sodium Carbonate in Air. Hugo Dubovitz (*Chem. Zeit.*, 1921, **45**, 890—891).—Commercial sodium carbonate almost always contains a quantity of sodium hydrogen carbonate, the carbon dioxide and water required for the formation of the latter being derived from the atmosphere. After about thirteen days' exposure to air, sodium carbonate may contain from 15 to 20% of the hydrogen carbonate; if the air is very moist and contains a large quantity of carbon dioxide, the conversion of the carbonate into the hydrogen carbonate may be complete. To estimate the amount of sodium hydrogen carbonate in sodium carbonate, a portion of the sample should be heated in a tube connected with a weighed calcium chloride tube; the loss in weight of the two tubes is a measure of the carbon dioxide in the hydrogen carbonate, whilst the gain in weight of the calcium chloride tube is due to the water formed by the decomposition of the hydrogen carbonate and to the moisture in the sample. W. P. S.

Recrystallisation of Metals. The Recrystallisation of Zinc. G. Masing (*Zeitsch. Metallk.*, 1921, **13**, 425—428).—On heating zinc that has been cold-worked, primary recrystallisation of the metal begins immediately throughout the mass without the formation of nuclei. As the temperature rises to 170—190° nuclei of secondary crystals begin to appear in the mass of primary crystals and these gradually increase in number and size if the heating is continued slowly until the whole of the metal consists of a mass of large secondary crystals which are coarser the lower the temperature of formation and the longer the heating. If the metal is subjected to a secondary deformation, the secondary crystal nuclei begin to form at 70°. [Cf. *J. Soc. Chem. Ind.*, 1921, 737A.] A. R. P.

Revision of the Atomic Weight of Zinc. II. Electrolytic Estimation of Zinc in Zinc Chloride. Gregory Paul Baxter and James Hallett Hodges (*J. Amer. Chem. Soc.*, 1921, **43**, 1242—1251; cf. A., 1916, ii, 327).—The atomic weight of zinc has been redetermined by means of the electrolytic estimation of the amount of zinc in zinc chloride. The method of analysis was the same as that previously used for the analysis of zinc bromide. The zinc chloride used was prepared as follows. Crude zinc was electrolytically transported through a concentrated solution of zinc bromide, and the crystalline sponge of pure zinc thus obtained was thoroughly washed with water and very dilute hydrobromic

acid. It was then immersed in dilute hydrobromic acid and treated with bromine and kept cold. The solution was kept over zinc sponge for three months to remove any traces of cadmium which might be present. The purified solution was fractionally crystallised, using only platinum apparatus. The purest crystals were fused in a platinum boat in a current of nitrogen and hydrogen bromide, dissolved in water, and filtered from traces of carbon and silica. The bromide was crystallised, dried, placed in a quartz boat, and fused in a current of chlorine, and the product used in the analyses. As a mean of eleven analyses, zinc chloride was found to contain 47·970% of zinc, which gives a mean atomic weight 65·372, or, rejecting four relatively low values, 65·379. This value is in good agreement with Richards and Rogers's value 65·376 (A., 1896, ii, 21) and Baxter and Grose's value 65·388 (loc. cit.) and indicates that the true atomic weight lies very close to 65·38.   J. F. S.

Revision of the Atomic Weight of Cadmium. V. Electrolytic Estimation of Cadmium in Cadmium Sulphate. GREGORY PAUL BAXTER and CARL HENRY WILSON (J. Amer. Chem. Soc., 1921, 43, 1230—1241; cf. A., 1916, ii, 327).—The atomic weight of cadmium has been redetermined by the electrolysis of anhydrous cadmium sulphate. Preliminary experiments with the hydrated salt showed that this salt generally contains a small amount of water above that required for the composition $CdSO_4,8/3H_2O$, and since such water cannot be removed, the hydrated salt is unsuitable for atomic weight determination. Anhydrous cadmium sulphate was prepared from the hydrated salt by heating at 200° in a current of air for two hours when most of the water was removed, the heating was then continued at 720° in a current of sulphur trioxide until a constant weight was obtained. After cooling, the product was heated at 200° for a further two hours to remove sulphur trioxide. The weighed sulphate was dissolved in water and electrolysed, using a weighed mercury cathode in the same way as previously described (loc. cit.). As the result of eleven analyses, the value 112·409 was obtained for the atomic weight, the extreme values being 112·328 and 112·437. The mean of the whole of the work of the author and his collaborators on the atomic weight of cadmium is 112·411. The preliminary experiments on the hydrated salt gave a value 112·04.   J. F. S.

Physical Chemistry of the Oxides of Lead. I. The Solubility of Lead Monoxide. SAMUEL GLASSTONE (T., 1921, 119, 1689—1697).

Theory of Smelting. IV. Equilibrium between Metalpairs and Sulphur. The System: Copper–Manganese–Sulphur. W. GUERTLER and K. L. MEISSNER (Metall. u. Erz, 1921, 18, 438—443; cf. this vol., ii, 402, 589). On melting manganese with copper sulphide, the mass separates into two layers, the upper consisting of manganese sulphide or of a eutectic of manganese and cuprous sulphides and the lower of pure copper or of mixed

crystals of copper and manganese, according to the proportions of both metals present. Manganese has, therefore, a greater affinity for sulphur than copper, and this affinity is not modified by the addition of iron. Thus, if to a mixture of molecular proportions of cuprous sulphide with 1 atomic proportion of manganese, iron is added, the mass separates into three layers, an upper layer of manganese sulphide, a middle layer of a eutectic mixture of manganese sulphide and iron, and a lower layer of copper more or less mixed with iron.　　　　　　　　　　　　　　　　　　A. R. P.

The Constitution of the Alloys of Copper with Tin. III. and IV. J. L. HAUGHTON (*J. Inst. Metals*, 1921, **25**, 309—330; cf. A., 1915, ii, 689).—A study of the equilibrium diagram of copper-tin alloys containing 30—100% of tin at temperatures below 250° by thermal curves and electrical resistance measurements. The alloy with 30·5% of tin shows no arrest between 150° and 250°. The alloy with 42·8% of tin shows a small arrest at about 190°. The alloy containing 57% of tin shows a greater arrest at 190° and in addition a slight arrest at about 210°. These two arrests are present in alloys containing 59% and 61% of tin. At 63% of tin the 190° arrest is pronounced and the 210° point has vanished and a new one has taken its place at 226°. As the percentage of tin increases the size of the higher arrest increases and the size of the lower arrest decreases, being barely perceptible at 90% of tin. The 210° arrest is not affected by the rate of heating whereas on rapid heating the 190° arrest will not show. After the 190° arrest has been suppressed, slow heating or cooling curves do not again show it until the sample has been annealed. Repeated heating and cooling at a slow rate bring about the disappearance of the 190° arrest from heating curves although it persists on the cooling curve. Electrical resistance measurements confirmed the presence of the 190° and 210° arrests. The arrest at 190° is caused by an allotropic change in the ϵ-constituent. The arrest at 226° is due to the solidification of the eutectic of the constituents ϵ and ζ. The latter is a dilute solid solution of copper in tin. The author cannot explain the cause for the appearance of the 210° arrest. A study of the equilibrium curve between 99 and 100% of tin showed that the solubility of copper falls off slightly with increasing tin content but that the slope of the curve is too small to show in the equilibrium diagram. In an appendix the author discusses the diagrams for copper–tin alloys suggested by other workers.　　　　　　　　　　　　　　　　CHEMICAL ABSTRACTS.

Stages in the Recrystallisation of Aluminium Sheet on Heating, and Birth of Crystals in Strained Metals and Alloys. H. C. H. CARPENTER and CONSTANCE F. ELAM (*J. Inst. Metals*, 1921, **25**, 259—280).—By heating for long periods at 220°, and for short periods at 250° and 300°, there is produced a general tarnishing of the surface, a granular structure, and a blurring of the original boundaries of the flattened crystals. The birth of new crystals in the old boundaries takes place in the early stages of recrystallisation at 250° and 300°. The structure obtained

after heating to structural equilibrium at a given temperature appears in two distinct forms. New evidence is offered in support of views already put forward (*ibid.*, 1920, **24**, 83) on the birth of crystals.   CHEMICAL ABSTRACTS.

The Function of Water of Crystallisation in the Behaviour of Permutite. A. GÜNTHER-SCHULZE (*Zeitsch. Elektrochem.*, 1921, **27**, 402—406).—Experiments were made to determine whether any relation exists between the water content of the permutite molecule and the mobility of the kation which is expressed in the readiness with which basic exchange takes place. The permutites of the alkali and alkaline-earth metals contain $5H_2O$, and it is generally considered that, of these, three are water of crystallisation and two "water of constitution." Experiments with potassium permutite, however, showed that the water content varies continuously according to the temperature and vapour pressure, and no distinction was found between the first three and the last two molecular proportions. The molecular volume of potassium permutite was determined at different stages of hydration, and it was found that the increase of volume per molecule of water was in proportion to the number of molecules of water added. So long as the permutite is not completely dehydrated, it can again be fully hydrated, but after ignition it takes up only about $1 \cdot 25H_2O$. The permutites of the metals copper, silver, chromium, and aluminium, formed by basic exchange from alkali metal permutites, contain from 6 to $8H_2O$; but when formed from ignited potassium permutite the water deficiency of this persists in the derived permutites. The mobility of the kation does not appear to be influenced by the water content. Ignited potassium permutite comes to the same point of equilibrium with a silver nitrate–potassium nitrate solution, for instance, as the fully hydrated permutite, but equilibrium is reached much more slowly, because, through partial sintering during ignition, the high porosity of the manufactured permutite is lost. The ignited permutite is very similar in character, in fact, to natural zeolites.   E. H. R.

Preparation of Colloidal Manganese Dioxide. EUSTACE J. CUY (*J. Physical Chem.*, 1921, **25**, 415—417).—The older methods for preparing colloidal manganese dioxide are enumerated and a new method is described. The method described consists in heating a $N/20$ solution of potassium permanganate to the boiling point and while stirring, adding concentrated ammonia solution at the rate of one drop every three to four minutes, until the solution has passed through a wine-red tint and become deep coffee coloured. At no period of the addition may the solution have a perceptible odour of ammonia. To test the complete absence of permanganate in the brown solution, a little is treated with sodium chloride solution which coagulates the colloidal manganese dioxide and leaves the characteristic colour of permanganate. The product contains only potassium hydroxide as an impurity, and as this substance has no action on the colloid, it may be left in the solution. The colloid is immediately coagulated by contact with paper and

parchment, and is therefore purified with great difficulty. It catalyses the decomposition of hydrogen peroxide and is perfectly stable in the presence of alcohol of all concentrations. J. F. S.

The **Electrolytic Production of Sodium and Potassium Permanganates from Ferromanganese.** ROBERT E. WILSON, W. GRENVILLE HORSCH, and MERRIL A. YOUTZ (*J. Ind. Eng. Chem.*, 1921, **13**, 763—769).—The electrolytic cells used in these experiments consisted of a cylindrical glass jar containing a porous porcelain cup which served as a diaphragm, the cathode (of 16-gauge sheet iron) being placed in the cup and the ferromanganese anode in the jar outside. Several cells were operated in series across a source of direct current. The circuit also contained an ammeter, a copper coulometer, and a rheostat. Arrangements were made for connecting a voltameter across any individual cell. The temperature of each cell was determined by means of a thermometer placed near to the anode. The average period of a run was five hours. The tabulated results of a large number of experiments are given, from which it is concluded that the most suitable anolyte is a solution of sodium carbonate, which gives a product uncontaminated by manganese, with the best efficiency and with the least expenditure of power. The percentage of manganese in the anode has little effect on the cell voltage, but increased manganese content gives increased current efficiency. With a 40% manganese anode (Spiegeleisen), practically no permanganate is produced. The commercial ferromanganese containing 80% of manganese was found to be the most suitable material. The presence of copper in the anode produced practically no effect, but 2% of cobalt reduced the efficiency almost to zero. The operating temperature should not be higher than about 10—20°, as increase of temperature lowers efficiency, increases the energy consumption, and gives rise to a " skin effect " which causes excessive voltages. A current density of about 6 amperes per sq. dcm. gives the minimum energy consumption. At lower current densities the current efficiency falls rapidly; at higher current densities it rises slowly but is accompanied by increased energy consumption. The effect of all variables such as current density, temperature, anolyte composition, etc., is stated to be due to the variations caused by these factors in the oxygen overvoltage, a high oxygen overvoltage being necessary for high current efficiencies in permanganate production. S. S. A.

Magnetic Determinations of A_0, A_1, A_2, and A_3 Points in Steels containing up to 4·8 per cent. of Carbon. TORAJIRÔ ISHIWARA (*Sci. Rep. Tôhoku Imp. Univ.*, 1920, **9**, 401—415; cf. A., 1913, ii, 222).—The specimens examined numbered twenty-two, and ranged from pure iron to steel containing 4·81% of carbon; the determinations were made by a magnetometric method and with a torsion balance, and the heating was effected in a vacuum. The results obtained are discussed fully, and are recorded in tabular form and also in a series of graphs. W. P. S.

Chemical Equilibrium between Iron, Carbon, and Oxygen.
A. MATSUBARA (*Trans. Amer. Inst. Mining Met. Eng.*, 1921, No. 1051, 52 pp.).—An investigation of (1) the equilibrium composition of the gas phase in the system: carbon monoxide–carbon dioxide–iron (containing 2 to 30% of oxygen) at 873°, 1070°, and 1175°; (2) the equilibrium composition of the gas phase in the systems (a) carbon monoxide–carbon dioxide–ferrous oxide (saturated with iron)–iron (saturated with ferrous oxide) and (b) carbon monoxide–carbon dioxide–ferrosoferric oxide (saturated with ferrous oxide)–ferrous oxide (saturated with ferrosoferric oxide) at several temperatures above 700°; (3) the equilibrium composition of the gas phase in the systems (a) ferrous oxide–iron carbide (Fe_3C)–carbon monoxide–carbon dioxide, and (b) iron–iron carbide–carbon monoxide–carbon dioxide in the range 700° to 1100°. The specific reactions considered are: (i) $3Fe_2O_3 + CO \rightleftharpoons 2Fe_3O_4 + CO_2$; (ii) $Fe_3O_4 + CO \rightleftharpoons 3FeO + CO_2$; (iii) $FeO + CO \rightleftharpoons Fe + CO_2$; (iv) $2CO \rightleftharpoons C + CO_2$; (v) $3Fe + 2CO \rightleftharpoons Fe_3C + CO_2$; (vi) $3FeO + 5CO \rightleftharpoons Fe_3C + 4CO_2$. The first period of carburising reaction apparently coincides with the latter, and a later period with the former of the last two reactions. There exist also transient equilibria between reactions (v) and (vi), (v) and (iii), (vi) and (iv). Equilibria at lower temperatures occur with a more oxidised form of the solid phase than at higher temperatures, even in the same carburising reaction. The limits of temperature and pressure for carburisation are determined from the experimental data. Above 1300° the carburising action of carbon monoxide does not occur; carburised iron is oxidised to a ferrous oxide–iron solid solution by pure carbon monoxide at 1 atmosphere pressure. Under 1 atmosphere pressure, at 1200°, neither carburisation nor decarburisation occurs in pure carbon monoxide; between 1200° and 1300°, iron containing carbon is decarburised by pure carbon monoxide, but iron containing oxygen may be carburised by the same gas, both reactions ending in the formation of oxygenated carboniferous iron proper to that temperature. Between 695° and 1200° a gas sufficiently rich in carbon monoxide will carburise iron; below 695°, no true carburisation can occur.   CHEMICAL ABSTRACTS.

Stereochemical Configuration of the Aquo-triammine and Diammine Cobalt Complex Salts. KICHIMATSU MATSUNO (*J. Coll. Sci. Tokyo*, 1921, **41**, 10, 1—27).—The absorption spectra of aqueous solutions of the eight aquo-cobaltammines,

$$\left[Co_{H_2O[2]}^{H_2O[1]} en_2 \right] Cl_3, 2H_2O; \quad \left[Co_{H_2O[6]}^{H_2O[1]} en_2 \right] Cl_3, 2H_2O;$$

$$[CoCl(H_2O)_2(NH_3)_3]SO_4; \quad [CoCl_2H_2O(NH_3)_3]Cl;$$

$$[CoCl_2(H_2O)_2(NH_3)_2]SO_4H; \quad [CoCl(H_2O)_3(NH_3)_2]SO_4,H_2O;$$

$[Co(H_2O)_3(NH_3)_3]Cl_3$ and $[Co(H_2O)_3(NH_3)_3]Cl_3$ have been measured over a wide range of concentrations. The electrical conductivity of six complex cobaltammines has also been measured at intervals over periods of time. From the results, the author has demonstrated the influence of the co-ordinated water molecules and has drawn the configurations of the compounds. Two new complex

compounds have been obtained, trans[Co(NH$_3$)$_3$(H$_2$O)$_3$]Cl$_3$ and [Co(NH$_3$)$_3$C$_2$O$_4$·NO$_3$]. The complex compound prepared by Werner by the action of silver nitrate on [CoClC$_2$O$_4$(NH$_3$)$_3$] and given the formula [Co(NH$_3$)$_3$C$_2$O$_4$(H$_2$O)$_2$]NO$_3$ is shown to have the formula [Co(NH$_3$)$_3$C$_2$O$_4$NO$_3$]H$_2$O. An explanation is given of the substitution reactions of the cobaltammines which have the radicles of strong acids in the nucleus. J. F. S.

Reduction of Chromium and other Difficultly Reducible Metals. H. C. P. WEBER (U.S. Pat. 1373038).—A mixture of chromic chloride with iron is heated to 700—1200° to produce metallic chromium and volatilise ferric chloride. If the iron is sufficiently finely divided, and a relatively low temperature is employed for reduction, chromium is obtained in finely divided form. If solid pieces of iron are used and the reaction takes place below the m. p. of the metals, a coating of chromium is formed on the pieces of iron. If an excess of iron is used and a sufficiently high temperature is employed, an alloy of chromium and iron is produced. Chlorides of chromium and nickel may be similarly reduced together to form alloys or mixtures with each other or with iron. Chromic oxide may be employed and converted into chloride with carbon and chlorine. The reduction process is advantageously carried out in a vacuum or in an inert atmosphere such as nitrogen. Other refractory metallic compounds may be similarly reduced and alloyed. CHEMICAL ABSTRACTS.

The Existence of Gaseous Hydrides of Zirconium and Thorium. ROBERT SCHWARZ and ERICH KONRAD (*Ber.*, 1921, 54, [*B*], 2122—2133).—The question of the existence of gaseous hydrides of zirconium and thorium is of considerable theoretical interest since, if producible, they would form exceptions to Paneth's rule (A., 1920, ii, 749). The preparation of volatile zirconium hydride has been claimed by Winkler (A., 1890, 1375), but denied by Wedekind (A., 1913, ii, 225), whilst preliminary experiments by Schwarz and Deissler (A., 1920, ii, 42) have pointed to its existence. The formation of thorium hydride is recorded by Klauber and von Mellenheim (this vol., ii, 206). Evidence of the existence of either hydride in the gaseous state has not now been obtained.

The experiments are performed by heating the pure respective dioxides with magnesium, dissolving the products in hydrochloric acid and leading the volatile and dried gases, mixed with purified hydrogen, through a series of strongly ignited Marsh tubes. In general, small mirrors are thus obtained which are shown to consist mainly of silicon; the presence of zirconium or thorium could not be detected in any instance. In addition to silicon hydride, the gases evolved contain small amounts of the hydrides of phosphorus and sulphur.

Reduction of the zirconium dioxide by magnesium is effected in iron crucibles which have been coated internally with an electrolytic deposit of nickel and are provided with a gas-tight iron lid so arranged that a current of hydrogen may be passed through the apparatus. Unsatisfactory results were obtained by heating the

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mixture in an electric furnace at about 1000°, or by its ignition by a thermite mixture or magnesium ribbon; satisfactory products are most readily secured by gradually heating the crucible almost to bright redness in a blowpipe flame.

All possible precautions are taken to eliminate the possibility that the non-observance of a metallic mirror is due to the rapid decomposition of the gaseous hydrides before reaching the Marsh tubes.   H. W.

Revision of the Atomic Weight of Bismuth. Analysis of Bismuth Chloride and Bismuth Bromide. O. HÖNIGSCHMID and L. BIRCKENBACH (*Ber.*, 1921, **54**, [*B*], 1873—1904).—A detailed account of work of a portion of which a preliminary notice has appeared previously (A., 1920, ii, 549).

Two series of analyses of bismuth chloride and bismuth bromide are recorded. In each series, the atomic weight is determined by two independent methods (gravimetric estimation of the ratios $BiCl_3 : 3AgCl$ and $BiBr_3 : 3AgBr$ and nephelometric measurement of the silver haloid dissolved in the mother-liquor and determination of the ratios $BiCl_3 : 3Ag$ and $BiBr_3 : 3Ag$ by gravimetric titration with the aid of the nephelometer). In all, eight independent mean values of the atomic weight are thus obtained, the extreme results being 208·98 and 209·00 on the basis $Ag = 107·88$. The values recorded previously (*loc. cit.*) are rendered slightly uncertain by the subsequent observation that the silver condensing tube used in the preparation of the water was giving small amounts of silver ions to the latter (the effect is due to access of laboratory air) and it is only possible to apply an estimated correction. The mean value of the six most trustworthy series is $Bi = 208·997$ or, in round numbers, 209·00; this is a unit higher than the international value previously adopted. The titrimetric values are regarded as the most trustworthy of all and twenty-two estimations are recorded in which the maximal difference in the individual results is 0·5 : 10000.

The experiments differ from the usual type of such determinations in that, in order to prevent the precipitation of basic bismuth salts, it is necessary to precipitate the chloride and bromide in $3N$- and $2N$-nitric acid solution respectively. This is shown to be without effect on the results by a special series of experiments with potassium chloride and bromide.

The recent determinations of the atomic weight of bismuth by Classen and Ney (thi. vol., ii, 119), which depend on the conversion of bismuth triphenyl to bismuth oxide, are criticised in detail. Recalculation of their figures on the basis $C = 12·001$ and $H = 1·0077$ gives the value $Bi = 208·91 \pm 0·05$ which is 0·09 lower than that calculated by the authors.   H. W.

Thermal Analysis of Binary and Ternary Alloys. J. WÜRSCHMIDT (*Zeitsch. Physik*, 1921, **5**, 39—43).—Cooling and heating curves have been produced for bismuth and tin and for a series of alloys of these metals. Similar experiments have been made with a series of ternary alloys of lead, bismuth, and tin and curves produced. The temperature measurements were made

with an iron–constantan thermo-element which made it possible to work with much smaller quantities of material than is usual. In the case of the binary alloys, the complete fusion diagram has been produced, and from this it is shown that the eutectic contains 46 atom % of bismuth and melts at about 140°. In the ternary alloys, the eutectic corresponds with the composition Bi_2SnPb and has a melting point of 96°. J. F. S.

The Chemical Properties of Alloys. G. TAMMANN (*Zeitsch. Metallk.*, 1921, **13**, 406—419).—The physical properties of binary alloys of two metals that form a continuous series of mixed crystals change regularly with varying composition, whereas their chemical properties alter suddenly when the atomic ratio of the metals present exceeds a certain well-defined limit, which may generally be expressed as $n/8$, where n, usually 1, 2, 4, 6, 7, rarely 3 or 5, is the number of atoms of the more noble metal in every 8 metal atoms. Thus, yellow ammonium sulphide blackens, in the cold, all alloys of gold and copper containing less than 50·8% of gold (atomic ratio 2/8 Au), whilst those richer in gold remain untarnished even after four years' immersion. Again, nitric acid dissolves silver completely from gold–silver alloys containing less than 52·5% of gold (atomic ratio 3/8 Au), partly from those containing 52·5—64·6 of gold (atomic ratio 4/8 Au), and not at all from those still richer in gold. Under certain conditions, however, these limits disappear, that is, the atoms of the active component tend to diffuse towards the surface, so that the surface layer falls below the limiting value. In the case of the copper–gold alloys, hydrogen sulphide, which behaves like ammonium sulphide at ordinary temperatures, attacks alloys richer in gold as the temperature rises, until, at 140° it blackens gold containing only 1% of copper. A theoretical explanation of the above phenomena, based on the space-lattice theory of crystal structure, is given in some detail and it is shown that it is possible to prepare what may be called " space-lattice isomerides " of alloys which behave differently towards certain reagents. The electrochemical behaviour of binary alloys may be studied by measuring the $E.M.F.$ of cells in which the electrolyte consists of a salt of the more electronegative metal from which one pole is made, whilst the other pole consists of different alloys of the two metals. If the composition of the latter is plotted against the voltage of the cell, the curve obtained for alloys in which inner diffusion takes place (for example amalgams) resembles a hyperbola concave to the axis of composition, whilst that obtained for alloys of metals (for example copper–manganese) which form a continuous series of mixed crystals, in general, runs close to this axis until a certain definite composition is reached, when it rises in a nearly perpendicular straight line to a constant voltage equal to that of a cell in which the poles consist of the two pure metals. Alloys of gold with copper and silver behave somewhat differently, the curve rising, after a certain percentage of gold, in a straight line to the value for pure gold, probably due to the deposition of a fine film of the latter on the surface of the alloy. Two metals that form several series of mixed

crystals, for example zinc and copper, give alloys that yield similar curves as manganese–copper except that there are a number of steps corresponding with the various series of mixed crystals, but these steps do not correspond with any definite atomic ratio between the elements. Gold–copper alloys, when made the anode in an electrolytic cell containing a solution of copper nitrate are attacked without evolution of oxygen if the gold does not exceed 29 atoms % copper dissolving from the alloy. If the voltage applied to a cell containing a large copper cathode and a small anode of gold–copper alloy is plotted against the amperage the curves for alloys containing 25—28 atoms % of gold show a peculiar double hump, whereas the curves for alloys richer or poorer in gold are roughly parabolic. The decomposition voltage of the series is at a maximum at nearly the same limit as that at which there is no attack by reagents, namely, 27 atoms % of gold, while polarisation is first noticeable with alloys containing 50 atoms % of gold. Alloys containing more gold behave in these two cases like pure gold.   A. R. P.

Preparation of Pure Platinum. EDWARD WICHERS (*J. Amer. Chem. Soc.*, 1921, **43**, 1268—1273).—Commerical platinum containing small quantities of rhodium, palladium, and iridium, as well as considerable quantities of iron, tin, and other base metals, may be freed from these impurities by four precipitations of ammonium platinichloride. The method consists in dissolving the metal in aqua regia, removing excess of nitric acid by repeated boiling with hydrochloric acid, and precipitating with ammonium chloride. The precipitate is drained on a Buchner funnel, stirred with a considerable volume of 15—20% ammonium chloride solution, and again drained; the washing is repeated three or four times. The washed precipitate is dried and ignited to sponge in an electrically heated muffle. The sponge is dissolved in aqua regia and the process repeated four times. The amount of platinum left in the mother-liquor does not exceed 1% of the platinum in the precipitate. The final precipitate is ignited to sponge in a porcelain dish over a gas flame, and during the reduction a current of hydrogen is passed over the material. The metal was tested for purity by spectroscopic examination and by measuring its thermo-electric effect against a very pure piece of Heraeus wire. The samples were melted to buttons in an oxy-hydrogen flame on a lime slab and then rolled into ribbons. Spectroscopically, the ribbons were found to be pure except for calcium and very often magnesium, but those which had been prepared by melting in an oxy-hydrogen flame containing an excess of oxygen contained less calcium than those prepared in the ordinary oxy-hydrogen flame. Strips prepared in the ordinary oxy-hydrogen flame gave considerable positive *E.M.F.* values against the standard wire at 1200°, whilst those prepared in the flame with excess of oxygen gave negative values varying from 2 to 38 micro-volts in the same circumstances. The calcium taken up by the platinum is in the form of metal, produced from the lime by the reducing atmosphere. The amount of calcium taken up by the platinum in the above-named circumstances can be considerable,

and in some cases the platinum is alkaline to moist litmus. The purest platinum yet obtained contains 0·0001% of calcium. Melting platinum in magnesia crucibles yields a brittle button which cannot be rolled, and in some cases the button was found to contain 3% of magnesium.   J. F. S.

Mineralogical Chemistry.

Nature and Chemical Composition of a Mineral containing Cobalt found at Katanga. A. SCHOEP (*Bull. Soc. chim. Belg.*, 1921, **30**, 207—212).—A colloidal mineral allied to heterogenite (cf. Frenzel, this Journal, 1872, 990) and schulzenite (cf. Maertens, A., 1896, ii, 529) and resembling lustrous anthracite in appearance, has been found embedded in malachite and chrysocolla. Its composition is estimated to be $3Co_2O_3,CoO,CuO,7H_2O$.   J. H. L.

The Chemical Constitution of Silicates. B. GOSSNER (*Centr. Min.*, 1921, 513—525).—A theoretical paper in which the author criticises current views as to the chemical constitution of silicates. Attempts to deduce from the chemical composition of a crystal the constitution of the corresponding molecular unit are fallacious. It is pointed out that the existence of complex silicates such as $(SiO_4)_3Al_2Ca_3$ or Si_3O_8AlK at the high temperatures at which the corresponding minerals were formed is most improbable, for the chemical affinities of silica and alumina, slight at ordinary temperatures, diminish at higher temperatures. For similar reasons, the existence in minerals of such radicles as $-Al(OH)_2$ is inconceivable. The author endeavours to show that, by postulating the existence of a limited number of simple stable silicates as molecular individuals, the structure of more complicated silicates can be explained as due to combinations of these. Without inquiring further into the nature of the combination of the simpler silicates to the more complex forms, this may be taken as similar to that existing in crystalline double salt or in solid compounds containing water of crystallisation. The simple silicates postulated are SiO_3Na_2, SiO_3Ca, SiO_3Mg, SiO_2,Al_2O_3, all of which can readily be obtained crystalline from the fused state. When water is a constituent of a silicate crystal, hydroxides such as $Ca(OH)_2$ or $Mg(OH)_2$ may be present, and, in certain circumstances, AlO_2H and AlO_3H_3, both of which are known in the crystalline state. From this point of view the composition of several groups of minerals is discussed, particularly in relation to the paragenesis of the minerals. As an example, in the alkali–lime–silicate group, the following formulæ are given :

Nepheline, $SiO_3Na_2,[SiO_2,Al_2O_3]$.
Leucite, $SiO_3K_2,[SiO_2,Al_2O_3],2SiO_2$.
Albite, $SiO_3Na_2,[SiO_2,Al_2O_3],4SiO_2$.
Anorthite, $SiO_3Ca,[SiO_2,Al_2O_3]$.

These formulæ bring out well the relationships between the minerals of this group, the fact that nepheline and anorthite have sharp melting points whilst the others have not, and that the former pair more readily undergo secondary changes in geological deposits, for instance into zeolites, whilst the others behave as if they were in a sense more saturated. A number of other groups are also discussed.   E. H. R.

Analytical Chemistry.

Application of the Immersion Refractometer to the Analysis of Aqueous Salt Solutions. C. A. CLEMENS (*J. Ind, Eng. Chem.*, 1921, **13**, 813—816).—Where n=the refractive index of solution, n_0=the refractive index of water of the same temperature, and c=grams of solute per 100 c.c. of solution, $n-n_0/c$ is a constant. Thus $c/n-n_0$ is a constant independent of temperature, unaffected by dissociation, hydration, and the formation of complexes, and represents the percentage by volume of salt equivalent to one division of the immersion refractometer scale. In determining the composition of mixtures of two salts, one of known and the other of unknown concentration, the percentage of the salt of known concentration divided by its refractive index factor gives in terms of scale divisions the effect on the refractive index due to that salt, and when this value is subtracted from the refractive index of the solution containing the two salts the remainder is equivalent to the refractive index of the salt of unknown concentration in aqueous solution. In the case of two salts both of unknown concentration the specific gravities of the solutions d_4^{20} were taken and the value for water was subtracted. The values thus obtained were then divided by the respective percentages by volume of salt in the solutions. This gave the effect of the addition of 1% of salt on the density of the solution at 20°. The density of a solution at 20° can be calculated by means of the factors thus obtained by multiplying the factor by the percentage of the salt and adding the value for water. By reversing the process, the percentage of salt can be found from the density. Knowing the refractive index of the solution and of water at the same temperature and d_4^{20} of the solution, the percentage by volume of the two salts can be calculated.   S. S. A.

Measurement of Hydrogen–Ion Concentration. G. W. MONIER-WILLIAMS (*Analyst*, 1921, **46**, 315—324).—The construction of an inexpensive apparatus, and the method of using it for the determination of hydrogen-ion concentrations, are fully described.   W. P. S.

Joint Use of Two Indicators in the Titration of Acids and Bases. J. L. LIZIUS (*Analyst*, 1921, **46**, 355—356).—The joint

use of two indicators, phenolphthalein and thymolphthalein, or methyl-red and thymol-blue, is recommended, since the colour changes denote either the approach of the end-point or the fact that the solution has been over-titrated.   W. P. S.

Rapid Electroanalysis. ARNOLD LASSIEUR (*Bull. Soc. chim.*, 1921, [iv], **29**, 754—780).—A lecture delivered before the French Chemical Society.   W. G.

System of Qualitative Chemical Analysis for the Positive Ions. CLAUD H. HALL, jun. (*Trans. Maryland Acad. Sci.*, 1921, 4, 8 pp.).—The first group is precipitated by means of red phosphorus instead of by hydrochloric acid; this serves to bring mercury entirely into this group and places all the lead in the second group. Thioacetic acid, or its ammonium salt, is substituted for hydrogen sulphide. In the alkali group, potassium is precipitated by means of phosphotungstic acid.   CHEMICAL ABSTRACTS.

Estimation of Water in Alcohols. TH. WIRTH (*Zeitsch. Deut. Oel-Fett. Ind.*, 1921, **41**, 147).—Five grams of calcium hydride granules are covered with xylene (previously dried by boiling with calcium hydride) and the mixture is boiled for a moment to dislodge air adhering to the solid; the air in the flask is displaced by pure dry carbon dioxide. The gas is admitted for the duration of the estimation at the rate of two bubbles per second, the exit tube leading to a gas burette containing potassium hydroxide solution. About 1 gram of the alcohol is drawn into the flask from a dropping funnel which is rinsed with 10 c.c. of xylene. Evolution of hydrogen, half of which is derived from the water according to the equation : $CaH_2 + H_2O + CO_2 = CaCO_3 + 2H_2$, begins immediately and is complete in forty-five minutes.   CHEMICAL ABSTRACTS.

Estimation of Hydrogen Peroxide by means of Stannous Chloride. SVEN HASSELSKOG (*Svensk. Farm. Tid.*, 1921, **25**, 149—150).—The method for the estimation of hydrogen peroxide proposed by Bertalan (A., 1916, ii, 393) is not trustworthy. There is not a single simple reaction involved as claimed. Two other by-reactions occur, namely : $SnCl_2 + xH_2O_2 \rightleftharpoons SnO_2, xH_2O + Cl_2 +$ $(x-2)O$ (see Zsigmondy, " Kolloidchemie," 2nd. ed.) and $2HCl + H_2O_2 \rightarrow 2H_2O + Cl_2$.   CHEMICAL ABSTRACTS.

Electrometric Estimation of Bromate, Dichromate, Nitrite, and Chloride Ions. W. S. HENDRIXSON (*J. Amer. Chem. Soc.*, 1921, **43**, 1309—1317; cf. this vol., ii, 411).—A continuation of previously published work (*loc. cit.*). In the present paper the author describes methods for the electrometric titration of the ions named in the title. The estimation of bromate by means of iodide and permanganate is effected as follows : A known excess of iodide solution is placed in the titration vessel, which is fitted with a mechanical stirrer and electrodes as previously described (*loc. cit.*) and sufficient 10N-sulphuric acid added to make the solution double normal. The bromate solution is then

added in such quantity that about 10% of the iodide is undecom-posed. The stirrer is started rotating and when the voltage becomes steady the excess of iodide is determined by titration with potassium permanganate solution. The method is accurate to about 0·08%, and the presence of chlorate ions does not influence the results. Iodide solutions may be directly titrated with bromate solution in the presence of 2N-sulphuric acid, the end-point being given by an abrupt rise in the potential. This estimation may be carried out in the presence of hydrochloric acid, but difficulties are experienced which become greater the greater the concentration of the acid and so render the accuracy in the presence of hydrochloric acid doubtful. Iodide may be titrated directly with dichromate in sulphuric acid solution of at least 2N strength, if sufficient time is allowed near the end point for the reaction to come to an end. The results in this case are accurate to 1 in 6300. Nitrous acid and nitrites may be estimated by the electrometric method as follows : a known quantity of permanganate solution is placed in the titration vessel, diluted, and 10N-sulphuric acid added to make the final concentration 1·5N. The stirrer is started and the nitrite solution slowly added so as to leave 5—10% of the permanganate unchanged. After about five minutes a known excess of iodide is added and the titration completed with permanganate solution. The method gives results which are equally as good as those obtained by the method of Laird and Simpson (A., 1919, ii, 242). The chloride ion may be estimated by adding an excess of a silver solution to a solution of chloride and stirring to coagulate the precipitate. The solution is filtered into the titration vessel, acidified with sulphuric acid, and treated with a measured excess of iodide solution, the excess of which is determined by titration with permanganate. The results are accurate to 1 part in 730 parts, but the method is involved and long.   J. F. S.

Estimation of Sodium Hyposulphite. JAMES HOLLINGS-WORTH SMITH (*J. Amer. Chem. Soc.*, 1921, **43**, 1307—1308).—The methods available for the estimation of sodium hyposulphite have been critically investigated with the object of finding a fairly rapid method in which it is unnecessary to ensure complete absence of air. The methods due to Ekker (A., 1894, ii, 479), Fradiss (A., 1900, ii, 44), and to Knecht and Hibbert (A., 1907, ii, 907) are all considered to be unsatisfactory for various reasons; the two first-named methods because of the action of air on the solutions and the last method because of the difficulty of preparing pure solutions of dyes of known composition and of the difficulty of working with solutions of titanous chloride. The method of Seyewetz and Bloch (A., 1906, ii, 578), which consists in oxidising the hyposulphite with an ammoniacal solution of silver chloride, according to the equation

$$Na_2S_2O_4 + 2AgCl + 4NH_4 \cdot OH = 2(NH_4)_2SO_3 + 2NaCl + 2H_2O + 2Ag,$$

and weighing the silver, suffers from two defects, first the gravi-metric procedure is slow, and, secondly, it is inaccurate because of the insoluble impurities in the hyposulphite which are held back by the filter and weighed with the silver. The author has modified

the process so that both defects are removed. The precipitated silver is filtered on a Gooch crucible, washed, and then dissolved in nitric acid and estimated by the Volhard method. A further modification consists in using silver nitrate instead of silver chloride. The modified method is carried out as follows : about 0·4 gram of hyposulphite is placed in a dry beaker and treated with double the theoretical quantity of ammoniacal silver nitrate solution. The hyposulphite dissolves and is immediately oxidised with the precipitation of metallic silver. The solution is filtered without warming on a Gooch crucible and washed free from silver salts with an ammoniacal solution of ammonium nitrate. The crucible is then placed in nitric acid and warmed to dissolve the silver and remove nitrous acid. The crucible is removed and the solution diluted and titrated with 0·1N-potassium thiocyanate solution. The method is rapid and accurate. J. F. S.

Estimation of Hyposulphites and Sulphoxylates. EDWARD L. HELWIG (*Amer. Dyestuff Reporter*, 1920, **7**, ii, 12—13).—Sodium hyposulphite is added in small quantities from a weighing bottle to 50 c.c. of a standard ammoniacal cupric sulphate solution (50 grams of crystallised copper sulphate and 10 c.c. of concentrated ammonia solution per litre) in a flask through which carbon dioxide is being passed, until the blue colour is discharged. The reaction is : $2CuSO_4 + 4NH_3 + Na_2S_2O_4 + 2H_2O = Cu_2SO_4 + Na_2SO_3 + (NH_4)_2SO_3 + (NH_4)_2SO_4$. An excess of hyposulphite causes the precipitation of 1/13·68 part of metallic copper. For the analysis of sodium sulphoxylate-formaldehyde ("formopon"), standard copper solution is added from a burette to an aqueous solution of the salt through which carbon dioxide is being passed; the liquid is then boiled and the copper solution added until a faint permanent blue colour is obtained. Basic zinc sulphoxylate-formaldehyde ("formopon extra") is dissolved in ammonia solution and estimated in a similar manner. CHEMICAL ABSTRACTS.

New Procedure for the Estimation of Arsenic. J. CRIBIER (*J. Pharm. Chim.*, 1921, [vii], **24**, 241—246).—A new method for the estimation of small quantities of arsenic is based on the intensifying and fixing action of potassium iodide on the yellow stain produced by hydrogen arsenide on mercuric chloride paper. The similar stains produced by the hydrides of antimony, sulphur, and phosphorus are not altered by potassium iodide in this way. The apparatus consists of a flask fitted with a vertical glass tube about 5 mm. in diameter and 30 cm. long. The lower end in the flask is drawn out to a dropping tube and a hole in the tube about 2·5 cm. from the bottom allows of the egress of the gas. For each estimation 8 grams of zinc and 60 c.c. of 20% sulphuric acid are used, and the arsenical solution, previously oxidised with a few drops of permanganate to convert sulphur and phosphorus compounds into non-reducible sulphuric and phosphoric acids, is added all at once. The lower part of the vertical tube contains a roll of filter-paper about 10 cm. long to absorb moisture carried up mechanically by the gas. The upper part of the tube contains the band of mercuric

chloride paper, 5 mm. wide and 12—15 cm. long, extending to within 2 cm. of the roll of filter paper. When all the arsenic is eliminated, which requires two to six hours or more, the test paper is treated with 10% potassium iodide solution, which, acting specifically on the arsenic stain, turns it brown, and at the same time renders it permanent to light and moisture. The arsenic is estimated by comparison of the stain with those produced by known quantities under similar conditions. From 0·0001 to 0·1 mg. can be estimated by the above procedure.   G. F. M.

Estimation of Carbon in Aluminium. J. A. SONDAL (*Tidskr. Kem.*, 1920, **17**, 234—245).—Carbon present in commercial aluminium in amounts varying between 0·012 and 0·087% is estimated by treating the metal with potassium cuprichloride solution and weighing the residue, or by an adaptation of the wet combustion method of Corleis. The oxidising mixture used contained for each gram of aluminium : 15 c.c. of saturated copper sulphate solution, 15 c.c. of saturated chromium trioxide solution, and 60 c.c. of a mixture containing by volume 5 parts of saturated chromium trioxide solution, 75 parts of concentrated sulphuric acid, 20 parts of phosphoric acid, and 35 parts of water. Solution of the metal is rapid and may be too violent at first.   CHEMICAL ABSTRACTS.

The Detection of Carbon Monoxide. C. R. HOOVER (*J. Ind. Eng. Chem.*, 1921, **13**, 770—772).—An absorbent, Hoolamite, (U.S. Pats. 1321061 and 1321062), is prepared by mixing together fuming sulphuric acid 53—56%, iodine pentoxide 10·6—12%, and pumice stone 33—35%. At ordinary temperatures carbon monoxide is oxidised by this reagent to carbon dioxide with liberation of iodine, which reacts with excess of sulphur trioxide present to form a green substance indicative of the presence of carbon monoxide, and varying in depth with concentration of the gas. On keeping or gentle warming the green colour changes to orange-yellow and disappears in a few minutes, so that the material can again be used as before until about twelve tests have been made, when the colour produced becomes irregular and a fresh supply of reagent is required. The colour produced in each case is compared with permanent colour standards prepared from a mixture of pumice granules with normal and basic copper acetate and chromium oxide. By this means a quantitative test can be made with gas mixtures containing up to 0·2% of carbon monoxide. Interfering gases such as an unsaturated hydrocarbons, hydrogen sulphide, etc., are first removed from a gaseous mixture by passing it through dry active charcoal. 0·005% of carbon monoxide can be detected by passing 500 c.c. of a gas mixture through a glass tube containing a column of Hoolamite 50 mm.×5 mm. A pocket size detector apparatus has been devised.   S. S. A.

Estimation of Potassium in the Presence of Sodium, Magnesium, Sulphates, and Phosphates. H. ATKINSON (*Analyst*, 1921, **46**, 354—355).—The method depends on the solubility of sodium and magnesium perchlorates, sulphates, and

phosphates in methyl alcohol. The mixture of the salts is evaporated with perchloric acid until fumes of the latter are evolved, a further quantity of the acid is added and the evaporation repeated, and 100 c.c. of methyl alcohol are then added. The mixture is boiled for about one hour, cooled, and, after eighteen hours, the potassium perchlorate is collected on a filter, washed with 50 c.c. of methyl alcohol containing 5% by vol. of perchloric acid, d 1·12, and then with 20 c.c. of ethyl alcohol. W. P. S.

Estimation of Sodium, Potassium, Calcium, and Magnesium, in Urine, Blood, and Fæces. FREDERICK F. TISDALL and BENJAMIN KRAMER (*J. Biol. Chem.*, 1921, **48**, 1—12, and 223—232).—Rapid methods are described for the estimation of these metals in blood, urine, and fæces. The quantities of material required for the complete analysis are 7 c.c. of blood, 50 c.c. of urine, and 2 grams of dried fæces. C. R. H.

Methods of Estimating Calcium in the Blood. Experimental Control of the Methods of Jansen and of Marriott and Howland. H. LABBÉ and G. DE TONI (*J. Pharm. Chim.*, 1921, [vii], **24**, 247—255).—The titrimetric method of Jansen (A., 1918, ii, 174) gives results of which the accuracy is by no means proportional to the delicacy and length of the procedure. At least three estimations in each case are necessary in order to obtain a mean value closely approximating to the actual figure, and as each experiment requires 10 c.c. of blood, the amount required is fairly considerable, especially if dealing with children. The colorimetric method of Marriott and Howland (A., 1916, ii, 269; 1918, i, 21), depending on the decolorisation of ferric thiocyanate by oxalates, is not sufficiently delicate, the variations in intensity of the colour being too slight and the readings therefore more or less arbitrary. The filtration of the minute quantities of calcium oxalate precipitate is also a weak point in the method and may lead to loss. G. F. M.

Behaviour of Ammonium Carbonate towards Magnessium. P. C. N. BROEKSMIT (*Pharm. Weekblad*, 1921, **58**, 1250—1251).—In group analysis, addition of ammonium carbonate causes the precipitation of a double carbonate with magnesium if the solution is not sufficiently dilute. S. I. L.

A New Method for the Evaluation of Zinc Dust. BULLNHEIMER (*Metall u. Erz*, 1921, **18**, 443—446).—The dust is ground until it passes through a 90-mesh sieve; 1 gram is shaken with 20 c.c. of water in a 300 c.c. Erlenmeyer flask, 20 c.c. of sulphuric acid (100 grams per litre) and 25 c.c. of 3% hydrogen peroxide are then added together, and the whole is allowed to remain with occasional stirring for four to eight minutes. The zinc particles should then be all dissolved, leaving only a loose metallic slime of lead, etc. Twenty c.c. of 40% sulphuric acid are then added and the excess of hydrogen peroxide estimated by titration with potassium permanganate solution (15 grams per litre) which has been standardised against sodium oxalate. For exact results, the above

quantities and procedure must be strictly adhered to, the solution of the zinc must not take more than ten minutes and the titration must be carried out immediately after this.   A. R. P.

Estimation of Small Quantities of Zinc. M. BODANSKY (*J. Ind. Eng. Chem.*, 1921, **13**, 696—697).—To estimate small quantities of zinc in foods, etc., a weighed portion of the substance is treated with sulphuric acid and nitric acid, incinerated, the ash dissolved in dilute hydrochloric acid, and the solution filtered and evaporated. The dry residue is dissolved in dilute hydrochloric acid, copper is removed as sulphide, and excess of hydrogen sulphide is expelled by boiling the solution; the latter is then neutralised with ammonia, treated with 10 c.c. of 50%, citric acid solution, boiled, small quantities of calcium carbonate are added until a precipitate of about 1 gram of calcium citrate has formed and the mixture is treated with hydrogen sulphide. After some hours, the precipitate is collected, washed with 2% ammonium thiocyanate solution, dissolved in hot dilute hydrochloric acid, the solution diluted to 45 c.c. and treated with potassium ferrocyanide solution. The turbidity obtained is compared with that produced by a known amount of zinc under similar conditions.   W. P. S.

Gravimetric Analysis. XIX. XXIV. Estimation of Cadmium. II. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1921, **34**, 466—467; cf. this vol., ii, 559).—The cadmium is precipitated as cadmium ammonium phosphate, $Cd(NH_4)PO_4,H_2O$, by the addition of a considerable excess of 20% diammonium hydrogen phosphate solution to a very faintly acid, hot, dilute solution of a cadmium salt containing about 2% of ammonium chloride. The precipitate, initially amorphous, becomes crystalline on keeping for an hour with occasional stirring, and after two hours, or the next morning if desired, it is collected, washed with 50 c.c. of cold, saturated cadmium ammonium phosphate solution, and finally with methyl alcohol, and dried for two hours at 100°, at which temperature the water of crystallisation is not lost. As a further check on the weight, the precipitate may be converted in the pyrophosphate by ignition in a platinum crucible. The corrections to be applied to the weight of $Cd(NH_4)PO_4,H_2O$ obtained are as follows : Weight of precipitate 0·2—0·3 gram, add 0·2 mg.; 0·1 gram, add 0·3 mg.; 0·05 gram, add 0·4 mg.; 0·01 gram, add 1·9 mg. The presence in moderate quantity of other ammonium salts, sodium or potassium chloride, etc., does not appreciably affect the accuracy of the estimation.   G. F. M.

Rapid Estimation of Copper or Iron in Aluminium-Copper or Aluminium-Iron Alloys. PIERRE HULOT (*Bull. Soc. chim.*, 1921, [iv], **29**, 836—837).—Two to five grams of the alloy, according to the expected copper or iron content, are treated with cold 20% sodium or potassium hydroxide. The aluminium rapidly dissolves and the iron or copper is deposited. The metallic deposit is washed thoroughly by decantation, dried, and weighed. The results may be confirmed in the case of copper by dissolving the

deposit in nitric acid and estimating the copper electrolytically. In the case of iron, the metal is dissolved in hydrochloric acid and estimated in the usual way by precipitation as ferric hydroxide.

W. G.

The **Estimation of Mercury in Organic Compounds.** Hugo Bauer (*Ber.*, 1921, **54**, [B], 2079—2081).—The method consists in a modification of the procedure proposed by Rupp (A., 1908, ii, 1073) and by Wöber (A., 1920, ii, 333).

The substance (0·2—0·3 gram) is weighed into a wide-necked Jena glass flask provided with a two-holed rubber stopper carrying a small dropping funnel and a glass tube leading to a Peligot tube containing about 5 c.c. of water. Concentrated sulphuric acid (10 c.c.) is run into the flask (if the substance is in aqueous solution it is preferable to add fuming sulphuric acid) followed by hydrogen peroxide solution (30%, 3—5 c.c.), which is added slowly and with constant agitation and intermittent warming until a colourless solution is obtained; this operation is usually complete in a few minutes. The contents of the flask and Peligot tube are rinsed into a small beaker, and concentrated ammonia is added in slight excess, after which the mixture is covered and heated at its boiling point for about three minutes to destroy the Caro's acid formed. Ten c.c. of approximately $N/5$-potassium cyanide solution are added to the cooled mixture, followed by 5 drops of potassium iodide solution (10%). Excess of potassium cyanide is titrated with $N/20$ silver nitrate solution. The titre of the potassium cyanide solution must be determined daily by diluting 10 c.c. of it with water (30 c.c.) adding a few drops of ammonia and potassium iodide, and titrating with $N/20$-silver nitrate.   H. W.

Estimation of Metallic Aluminium and of Aluminium Oxide in the Commercial Metal. Julian H. Capps (*J. Ind. Eng. Chem.*, 1921, **13**, 808—812).—The metal is dissolved in sodium hydroxide or in acid in a special apparatus and the hydrogen liberated collected in a measuring burette where its volume, temperature, and pressure may be read. The volume of gas is equivalent to unoxidised aluminium, together with whatever iron is present when an acid reagent is used, or with the silicon when sodium hydroxide is used. The amount of the oxide content is calculated by difference from the estimated total aluminium present.

S. S. A.

Separation of Aluminium from Glucinum. Hubert T. S. Britton (*Analyst*, 1921, **46**, 359—366).—A solution of salts of the two metals, containing not more than 0·3 gram of glucina and 4 gram of alumina, is evaporated to a volume of about 25 c.c., cooled, and 24% sodium hydroxide solution is added in quantity just sufficient to re-dissolve the precipitated hydroxides. The mixture is then diluted to 500 c.c., boiled for forty minutes, the precipitated glucinum hydroxide collected on a filter, washed, ignited, and weighed. The filtrate is acidified with hydrochloric acid and the aluminium precipitated as hydroxide by the addition of ammonia.   W. P. S.

Colorimetric Estimation of Iron in Silicates with Ammonium Thiocyanate. JOSEF MATEJKA (*Chem. Listy*, 1921, **15**, 8—13; cf. Thomson, T., 1885, **47**, 493).—One to 2 c.c. of a standard iron solution (containing ferrous iron equivalent to 0·01 gram of ferric oxide per litre of 0·5% sulphuric acid), 8 c.c. of a mixture of 1 part of 10% nitric acid with 3 parts of 10% citric acid solution by volume, and 8 c.c. of 10% ammonium thiocyanate solution are diluted to the 20 c.c. mark in a colorimetric tube. Two similar tubes contain similar quantities of the same solutions, with the exception of the iron, diluted to about 19 c.c. The solution of the pyrosulphate fusion of the silicate in 0·5% sulphuric acid, having been diluted to 250 c.c., is added drop by drop to one tube until equivalent coloration is attained; on repeating the process, it is necessary that the final volume in the tube should be exactly 20 c.c. It is essential that the thiocyanate should be present in excess, and that its concentration should be the same in both tubes (cf. Tatlock, A., 1888, 90). Potassium sulphate and potassium hydrogen sulphate cause a reduction of the intensity and change the colour from pink to orange. Sodium, magnesium, calcium, and titanium chlorides and aluminium salts have a detrimental effect. The interference of all these salts is, however, inappreciable if the solution to be tested is sufficiently acidified with nitric and citric acids before the addition of thiocyanate. The method is equally as satisfactory as that of Lunge (*Zeitsch. angew. Chem.*, 1886, 3).   CHEMICAL ABSTRACTS.

A Simple, Exact, and Rapid Electrolytic Estimation of Cobalt in Ammoniacal Solution and its Application to Cobalt Nitroso-β-naphthol. K. WAGENMANN (*Metall u. Erz*, 1921, **18**, 447—449).—Cobalt may be rapidly and accurately deposited electrolytically on a rotating double platinum gauze cathode with a current of 5 amperes from a solution containing 5 grams of ammonium chloride, 30 c.c. of strong ammonia, and not more than 0·1 gram of cobalt as sulphate in a bulk of 125—150 c.c. In order to obtain bright, strongly adhering deposits, the cathode is rotated at 600—1200 revolutions per minute and 0·8—1·0 gram of hydrazine sulphate is added a little at a time during the electrolysis, which is complete in forty to forty-five minutes. Precipitation of cobalt with nitroso-β-naphthol and direct ignition of the precipitate to Co_3O_4 usually yields slightly high results due to inclusion of traces of iron, alumina, and copper, if present. The ignited oxide may be dissolved in fused alkali hydrogen sulphate, and the solution treated with ammonia and ammonium chloride and electrolysed as described above.   A. R. P.

Volumetric Estimation of Tin with Potassium Bromate. V. VELICH (*Chem. Listy*, 1921, **15**, 5—8, 38—41, 56—59).—The method as proposed by Fichter and Müller (A., 1913, ii, 34) is more fully developed. The reduction of solutions of stannic chloride in preparation for titration is best conducted in a closed flask, provided with a Fresenius stopper, an inlet tube for the addition of liquids, and an inlet tube for the continuous passage of carbon

dioxide. Aluminium is the best reducing agent, but in the estima-
tion of tin in alloys the presence of nickel during the reduction with
aluminium aids materially. Metals which are precipitated during
the aluminium reduction and do not redissolve in hydrochloric acid
are removed by filtration through an asbestos mat under reduced
pressure and in an atmosphere of carbon dioxide to prevent re-
oxidation. It is best to use a 0·2N-solution of potassium bromate,
kept in an atmosphere of carbon dioxide, for the titration. Various
indicators (oxazines, thiazines, and azines) were tried. Capri-blue
(L) is the most suitable for this reaction. The above method gives
satisfactory results for the estimation of tin in relatively pure
preparations and in alloys if these contain less than 0·3% of iron.

CHEMICAL ABSTRACTS.

**Estimation of Vanadium in Ores and Metallurgical
Products.** R. B. SCHAAL (J. Ind. Eng. Chem., 1921, **13**, 698—
699).—From 1 to 5 grams of the ore are boiled with 60 c.c. of hydro-
chloric acid, 5 c.c. of nitric acid and 2 c.c. of hydrofluoric acid are
then added and the mixture is evaporated to dryness; in the case
of ferrovanadium, a similar procedure is used to obtain the metal
a solution, but the hydrochloric acid is added after the other acids;
steel is dissolved in hydrochloric acid and the solution evaporated
with the addition of nitric acid. The residue obtained as described
s twice evaporated with the addition of hydrochloric acid, then
dissolved in hydrochloric acid, and the solution diluted and filtered.
The filtrate is treated with 60 c.c. of 15% ammonium phosphate
solution and ammonia is added until a precipitate of ferric phosphate
s formed; the latter is dissolved in a slight excess of hydrochloric
acid, the whole mixture is diluted to 300 c.c., and titrated with
standard potassium permanganate solution. W. P. S.

Solidifying Rate of Paraffins. K. FRICKE (Chem. Zeit., 1921,
45, 891—892).—To ascertain the suitability of solid paraffins for
candle-making, the author determines the solidifying rate or period
required for a melted paraffin to form a mass sufficiently hard to
support a given weight. One hundred grams of the paraffin are
melted at 65° and poured into a metal dish, 11 by 6 cm. and 3·5 cm.
in depth, and containing a thermometer. As soon as the first signs
of solidification are noticed, the time is noted and after a further
fifty-five minutes the lower end of an iron rod, 19 cm. square and
weighing 205 grams, is placed on the surface of the paraffin 2·5 cm.
from the side of the dish. The rod is supported vertically and
carries a weight of 2 kilos. If the end of the rod sinks into the
paraffin, the test is made again after five minutes, and so on, until
the depression made by the rod is negligible. A suitable paraffin
will solidify to this consistence within sixty-five minutes.

W. P. S.

Detection and Estimation of Coal-tar Oils in Turpentine.
V. E. GROTLISCH and W. C. SMITH (J. Ind. Eng. Chem., 1921, **13**,
791—793).—One hundred c.c. of the turpentine are saturated with
hydrogen chloride at a low temperature, the pinene hydrochloride

formed is separated by filtration, and the filtrate is distilled under reduced pressure until about 25 c.c. of distillate have been obtained: any tar-oils (toluene, xylene, and commercial solvent naphtha) present are thus concentrated in this distillate. The latter is added slowly to 100 c.c. of sulphuric acid containing 4% of free sulphur trioxide, the mixture is then heated at 70° for twenty minutes, cooled, diluted with water, and distilled with steam. Pure turpentine yields about 0·5 c.c. of yellow oil, n_D^{20} above 1·500; if mineral oil is present it is recovered at this point and is identified by its odour. When oil ceases to distil, the steam supply is disconnected and the mixture distilled directly, warm water being added drop by drop at such a rate that the temperature of the mixture rises gradually. Hydro-lysis of the sulphonated hydrocarbons commences at 115° and the free hydrocarbon distils; the distillation is stopped when the temperature approaches 170°. The volume of oil recovered in the distillate is multiplied by 2·2 to obtain the percentage amount of coal-tar oils in the sample, and these oils may be identified by the usual tests (nitration, etc.). The method is not trustworthy in the case of wood turpentines as the use of high temperatures in the distillation of the wood converts a portion of the terpenes into cyclic hydrocarbons.   W. P. S.

Estimation of Volatile Alcohols. AD. GRÜN and TH. WIRTH (*Zeitsch. Deut. Oel-Fett. Ind.*, 1921, **41**, 145—147).—To 0·5 to 1 gram of the sample in a 100 c.c. flask are added 5—10 c.c. of lauryl chloride prepared by distilling a mixture of lauric acid with phosphorus trichloride or pentachloride. The flask is plugged with cotton-wool, kept at about 60° for one-half to three hours, the contents are then shaken with 50 c.c. of water, boiled for one minute, cooled, extracted with ether, the free lauric acid is neutralised, and the ester quanti-tatively hydrolysed with potassium hydroxide. Simple, readily volatile alcohols can be accurately estimated, but such substances as geraniol and methylnonylcarbinol require to be kept for three hours at 60°. Secondary alcohols the hydroxyl group of which is attached to a ring carbon atom, for example, menthol, and tertiary alcohols do not, however, yield satisfactory results.
                                                CHEMICAL ABSTRACTS.

Estimation of Alcohols and Phenols in Ethereal Oils by Esterification with Pyridine. H. W. VAN URK (*Pharm. Week-blad*, 1921, **58**, 1265-1269).—Verley and Bölsing's method (A., 1902, ii, 54) has been examined for menthol, eugenol, and santal oils. In no case does the method give very exact results, but given conditions under which quick determinations may be made for santal oil and eugenol with fair approximation.   S. I. L.

A Method for the Estimation of Sugar in Normal Urine. STANLEY R. BENEDICT and EMIL OSTERBERG (*J. Biol. Chem.*, 1921, **48**, 51—57; cf. also A., 1918, ii, 246).—By elimination, by the use of acetone, of the confusion due to the presence of creatinine, the picric acid method of sugar estimation of Lewis and Benedict (A., 1915, ii, 111) is made applicable to urine. The addition of acetone

destroys the colour produced by creatinine, whilst leaving unaffected that due to the sugar. C. R. H.

Estimation of Lactose in the Presence of other Reducing Sugars. L. Le Grand (*Ann. Falsif.*, 1921, **14**, 268—269).—In using Barfoed's method (this vol., ii, 355) for the estimation of lactose in milk, the sugar solution should be diluted so that the concentration of alkali or alkaline-earth salts does not exceed 0·1%; when these salts are present in greater concentration, basic salts are precipitated and interfere with the estimation. W. P. S.

Revision of the Optical Method for Analysing Mixtures of Sucrose and Raffinose. C. A. Browne and C. A. Gamble (*J. Ind. Eng. Chem.*, 1921, **13**, 793—797).—Owing to the change in the Herzfeld divisor of the Clerget formula for estimating sucrose from 142·66 to 143, a revision of the Creydt formula for analysing mixtures of sucrose and raffinose is necessary. On the basis of the invert factor −0·33 for sucrose and +0·514 for raffinose, and 1·852 as the ratio of the specific rotation of sucrose to that of raffinose, the percentages of sucrose (S) and of raffinose (R) in a mixture are found by the formulæ : $S = 0.514$, $P - P'/0.844$, and $R = 0.33\ P + P'\ 1.563$, where P and P' are the direct and invert polarimetric readings at 20° of a normal (sucrose) weight solution of the mixture. General formulæ, applicable at all temperatures, are as follows : $S = P(0.478 \times 0.0018t) - P'(1.006 - 0.0003T)/(0.908 - 0.0032t)$ $(1.006 - 0.0003T)$ and $R = P(0.43 - 0.005t) + P'(1.006 - 0.0003T)/(1.681 - 0.0059t)$ $(1.006 - 0.0003T)$, where T is the temperature of the direct polarisation and t that of the invert polarisation. W. P. S.

The Use of Taka-diastase in Estimating Starch. Edward Horton (*J. Agric. Sci.*, 1921, **11**, 240—257).—The results of much experimental work on the estimation of starch by hydrolysis with taka-diastase are recorded, and show that the method is not always trustworthy. The quantity of enzyme suggested in the original method (Davis and Deisch, A., 1914, ii, 588) seems insufficient. Various commercial samples of the enzyme gave unsatisfactory results, and samples were prepared by the growth of *Aspergillus oryzæ* on sterile bran and on Munter's medium. The activity of the enzyme so prepared increased until the seventh day of growth and then declined. The use of asparagine as the source of nitrogen in the medium tends to produce a more active enzyme. On the whole, laboratory prepared samples gave no better results than commercial ones. Discordant figures are obtained if different classifying agents are used previously to the final sugar estimation. The addition of malt diastase does not increase the total starch figure, but raises the ratio : dextrose/maltose. The cause of the unsatisfactory results is not clear, but although evidence is somewhat conflicting, the theory that it is due to the persistence of dextrins has the greater weight. Control experiments with the enzyme used should be made on pure starch with each set of estimations. Results on this basis are fairly trustworthy. A. G. P.

Precipitation of Solid Fatty Acids with Lead Acetate in Alcoholic Solution. E. TWITCHELL (*J. Ind. Eng. Chem.*, 1921, **13**, 806—807).—The following procedure is recommended for the estimation of solid fatty acids in a mixture of fatty acids. Ten grams of the fatty acids from an oil, or 2 grams of the fatty acids from a fat, are dissolved in 95% alcohol, the solution is boiled, and 1·5 grams of lead acetate dissolved in boiling alcohol are added; the total volume of alcohol used should be 100 c.c. The mixture is cooled slowly to 15°, and, after about eighteen hours, the precipitate is collected on a filter and washed with alcohol until the filtrate ceases to give a turbidity when diluted with water. The precipitate is now dissolved in 100 c.c. of boiling alcohol containing 0·5 c.c. of acetic acid, the solution cooled, and the precipitate again collected, washed, transferred to a separating funnel, and shaken with ether and nitric acid ; the ethereal solution is separated, washed, evaporated, and the residue of fatty acids weighed. Fatty acids from different oils yielded the following quantities of solid fatty acids : Cotton-seed oil, 23·13% ; soja bean oil, 17·01% ; olive oil, 10·93% ; earth-nut oil, 16·58% ; lard, 40·02% ; partly hydrogenated cotton-seed oil, 50·62% ; tallow, 53·62%. The iodine value of the solid fatty acids was less than 1·0, except in the case of the hydrogenated cotton-seed oil (42·21) and the tallow (4·38). W.P.S.

Identification of Tartaric Acid in Wines. L. MATHIEU (*Ann. Falsif.*, 1921, **14**, 281—283).—Amyl alcohol extracts a portion of the free tartaric acid from wine, but not potassium hydrogen tartrate or calcium tartrate. Twenty c.c. of the wine are shaken with 20 c.c. of amyl alcohol, the latter is separated and shaken with 20 c.c. of water, and this aqueous extract is evaporated to dryness; the residue obtained is dissolved in 5 c.c. of water and the solution is treated with one drop of calcium chloride solution (15 grams of calcium chloride and 40 grams of ammonium chloride per litre) and 2 c.c. of *l*-ammonium tartrate solution. A precipitate of calcium racemate forms at once if the wine contained 0·5 gram. or more, of free tartaric acid per litre.   W. P. S.

Rapid Method for the Estimation of Hippuric Acid in Urine. F. B. KINGSBURY and W. W. SWANSON (*J. Biol. Chem.*, 1921, **48**. 13—20).—The authors describe a modification of the method of Folin and Flanders (A., 1912, ii, 396, 501) for the estimation of hippuric acid, by which, without sacrificing accuracy, the time necessary for the estimation is reduced from nine hours to between two and three hours.   C. R. H.

Determination of Watering and Creaming in Samples of Altered Milk. G. ANDOYER (*Comp. rend.*, 1921, **173**, 588—589).—It is shown that the coagulum of sour milk, when freed from fat and mineral matter, contains 15·6% of nitrogen. Thus the method of Kling and Roy for the analysis of samples of sour milk may be modified. The sample, after the addition of a little acetic acid, is filtered on a tared filter and washed with water. The coagulum is dried, extracted with ether, the fat being subsequently recovered and weighed, again dried, weighed, and incin-

crated. In the filtrate and washings the total ash and the soluble nitrogen are determined. From these data the percentages of fat, casein, and ash in the original milk can be calculated and any adulteration detected.　　　　　　　　　　　　W. G.

Detection of Formaldehyde by Resorcinol and Sulphuric Acid. ROBERT COHN (*Chem. Zeit.*, 1921, **45**, 997—998).—Krauss and Tampke's method (A., 1921, ii, 466) for the simultaneous detection of tartaric, oxalic, and formic acids by resorcinol and sulphuric acid has the disadvantage that the reaction is much more sensitive for the detection of tartaric acid than it is for the detection of oxalic or formic acid, and, consequently, it cannot always be applied for the detection of formic acid in food. In order to determine whether the formic acid reaction is influenced by the presence of other organic preservatives which are volatile with steam, the behaviour of formaldehyde with resorcinol and sulphuric acid was examined, and it was found that this reagent is very sensitive for the detection of formaldehyde. Two c.c. of 0·1% aqueous pure resorcinol solution are shaken with an equal volume of the distillate to be tested and about 2 c.c. of concentrated sulphuric acid are then added so as to form a layer below the solution. In the presence of formaldehyde a ring of white flocks with a violet-red coloured base is formed at the junction of the two liquids. After some time, the zone of white flocks increases upwards and a red precipitate, insoluble in water, separates. The reaction is immediate when the solution contains 0·01 gram of formaldehyde per 100 c.c., and is still distinct with only 0·05 mg. of formaldehyde. In the latter case, the violet-red ring may be faint, but the separation of the characteristic white flocks, which increase in quantity on keeping, is distinct. In presence of formic acid, oxalic acid, and tartaric acid, the ring of white flocks with a violet-red coloured base is formed first, although the violet-red colour may be masked by the brown formic acid ring; below this is the blue oxalic acid ring, and when the lower part of the tube is heated carefully, the deep red tartaric acid ring is formed at the bottom. When the test is carried out as described above with other aldehydes or their derivatives, a characteristic zone of white flocks is also produced, but a different coloured ring is formed at its base. Thus, benzaldehyde gives an intense yellow, acetaldehyde deep green, hexamethylene-tetramine greenish-brown, and dilute furfuraldehyde solution black-violet.　　　　　　　　　　　　　　F. M. R.

Separation of Aliphatic Amines from one another and from Ammonia. HARTWIG FRANZEN and ARTUR SCHNEIDER (*Biochem. Zitsch.*, 1921, **116**, 195—207).—For the investigation of the volatile bases of plants, a method for their quantitative separation is necessary. This can be effected as follows. Ammonium chloride and monomethylamine hydrochloride are insoluble in chloroform, whilst the hydrochlorides of di- and tri-methylamines are soluble. The ammonia and monomethylamine can be separated by addition of yellow mercuric oxide, which, provided the ammonia be not greatly in excess of the methylamine, combines with ammonia

alone. Di- and tri-methylamines can be separated by treatment with iodine in potassium iodide solution, which precipitates the trimethylamine as periodide.   H. K.

Behaviour of Nevralteine with Quinine Salts : Easy Method for its Identification. MARIO CARDINI (*Boll. Chim. Farm.*, 1921, **60**, 253—258).—The following reaction has been tested with all the antipyretics at present in use, and is found to be given only by nevraltcine (sodium *p*-phenetidinomethanesulphonate) : A small quantity (0·02 gram) of the substance and 0·01 gram of quinine hydrochloride or sulphate are treated together in a porcelain dish with a drop of water, a characteristic reddish-yellow coloration being obtained with nevralteine.   T. H. P.

Rapid Estimation of Carbamide in Urine, Blood, and other Physiological Fluids. H. STROHMANN and S. FLINTZER (*Zentr. inn. Med.*, 1921, **42**, 545—562; from *Chem. Zentr.*, 1921, iv, 493—494).—An examination of the methods of Folin and his co-workers (A., 1919, ii, 308). Difficulties in the hydrolysis by means of urease may be avoided by using smaller amounts of material (= about 0·2 gram of carbamide nitrogen) and working at greater dilutions. On account of the errors consequent on the small amounts of nitrogen to be estimated, the older method of Marshall (A., 1913, ii, 640) was tried. It gave more concordant results but demanded longer time. Using 10 c.c. of blood filtrate (instead of 5 c.c. as in Folin's method), the liquid may be nesslerised directly after hydrolysis if the same amount of ferment extract is added to the liquid used for comparison. The method to be adopted for the preliminary removal of protein will vary according to the liquid under examinatio an I the amount of protein present.   G. W. R.

Typical Reaction for the Differentiation of Carbazole Derivatives. A. V. BLOM (*Helv. Chim. Acta*, 1921, **4**, 625).— A number of examples are quoted to show that the colour developed on the addition of nitric acid to a solution of a derivative of carbazole is characteristic, and serves as an excellent criterion of purity.   J. K.

Comparison of Methods for Estimation of Uric Acid in Blood. PIETRO BIFFI (*Riv. osp.*, 11, 29—40; from *Chem. Zentr.* 1921, iv, 493).—The methods of Ludwig-Salkowski, Schittenhelm Schneller, Kowarski (piperidine), and Aufrecht (hydroxyl esti mation of ammonium urate) for the estimation of uric acid in blood were compared in cases of pathological bloods. The agree-ment was unsatisfactory, but the first two gave the most concordant results. The second method would appear to be the most trust-worthy. A modification of the Kowarski method (precipitation of the proteins by sulphosalicylic acid, transformation by means of ammonium chloride into ammonium urate, and, after washing with ethyl alcohol–acetone, estimation of the ammonia) gave passable results, but was less accurate than the methods first named.   G. W. R.